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Soil organic matter and metolachlor sorption characteristics as affected by soil management.

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SOIL ORGANIC MATTER AND METOLACHLOR SORPTION CHARACTERISTICS AS AFFECTED BY SOIL MANAGEMENT

A Dissertation Presented

By

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ABSTRACT

SOIL ORGANIC MATTER AND METOLACHLOR SORPTION CHARACTERISTICS AS AFFECTED BY SOIL MANAGEMENT

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Soil organic matter (SOM) plays an essential role in agriculture and in environments. It influences the productivity and physical well-being of soils. Therefore, it is important from both an economic and environmental standpoint to determine how agricultural practices will affect SOM and the biological cycling of carbon. Based on the changes of SOM characteristics, we further investigated the sorption dynamics and mechanisms of organic compounds in soil and SOM fractions under different soil managements. Several experiments were conducted and the results and conclusions were summarized as below. Long-term tillage experiment was initiated in 1979 at Clemson University Pee Dee Research and Education Center (Darlington, SC). Cover crop experiment was conducted in the Connecticut River Valley at the Massachusetts Agricultural Experiment Station in South Deerfield, Massachusetts (since 1990). Cross-Polarization Magic-Angle-Spinning (CPMAS) and Total Sideband Suppression (TOSS) solid-state ^{13}C Nuclear Magnetic Resonance (NMR) and Diffuse Reflectance Fourier Transform Infrared (DRIFT) spectroscopic

techniques were used to identify the structural and compositional changes of SOM. Metolachlor sorption experiments (3 days) were conducted using a batch-equilibrium method. Three desorption steps were carried out for a total of 9 days in a sequential decant-refill steps following the sorption experiment. Our NMR results indicated that humic acid (HA) from rye alone cover was more aromatic and less aliphatic in character than other cover crop systems without nitrogen fertilizers. Based on the DRIFT peak height O/R (reactive/recalcitrant) ratios, the highest ratio was found in the HA from vetch/rye system with nitrogen fertilizer. Compared to conventional tillage (CT), conservation tillage (CnT) held a higher SOM and light fraction (LF) in the surface layer (0-5 cm). Aromaticity of HA increased with soil depth in both tillages. Conversely, the aliphatic-C content decreased with soil depth. However, the aromaticity of HA in CT was higher than that of CnT in the top soil (0-5 cm). Sorption nonlinearity (N) of metolachlor and hysteresis were dependent on the structure and composition of SOM. These results showed that agricultural practices not only changed the structure of SOM, but also changed the pesticide sorption behavior in the soil.

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LIST OF ABBREVIATIONS

ANOVA: analyses of variance

CPMAS: cross-polarization magic-angle-spinning

CnT: conservation tillage

CT: conventional tillage

DRIFT: diffuse reflectance Fourier transform infrared spectroscopy

ESR: electron spin resonance

FA: fulvic acid

FTIR: Fourier transform infrared spectroscopy

HA: humic acid

HFB: hexafluorobenzene

HOCs: hydrophobic organic compounds

HSs: humic substances

IHSS: international humic substance society

LF: light fraction

O/R ratio: reactive/recalcitrant (functional groups)

SOC: soil organic carbon

SOM: soil organic matter

TCN: total combustible nitrogen

TOSS-NMR: total sideband suppression nuclear magnetic resonance

XRD: X-ray diffraction

CHAPTER 1

LITERATURE REVIEW

1.1 Introduction

Soil organic matter (SOM) is linked to desirable soil physical, chemical, and biological properties and is closely associated with soil productivity (Stevenson, 1994; Wattel-Koekkoek et al., 2001). Recent research has also recognized SOM as a central indicator of soil quality and health. Thus, characterization of SOM is valuable for identifying the overall quality of soils.

It is well known that agricultural management practices have significantly affected soil productivity and other organic-matter-dependent soil properties (Cheshire et al., 1990; Campbell et al., 1999; Willson et al., 2001). From an agronomic point of view, organic matter has often been partitioned into two major pools: "active (labile)" and "stable." It is well established that the labile components of SOM change and reach a new steady state more quickly in response to management variation than total organic matter (Eghball et al., 1994; Wander et al., 1994; Gregorich, 1996). Active SOM refers to a heterogeneous mix of living and dead organic materials that are readily circulated through biological pools. It is a major soil nutrient reservoir. Balance between decay and renewal processes in this pool controls nutrient availability and SOM status, i.e., determines whether organic matter is aggrading or degrading overall (Wander et al., 1994). Because organic, sustainable, and low-chemical-input systems rely increasingly on soil nutrient cycling mechanisms, it is crucial to understand the relationships between active SOM, total SOM, and nutrient retention and supply characteristics.

SOM influences soil characteristics such as water infiltration rate, water hold capacity, nutrient cycling, and pesticide sorption (Fliebbach and Mader, 2000; Wander and Yang, 2000). The tillage systems affect SOM dynamics. Conservation tillage management practices are known to increase levels of SOM. However, SOM changes may depend upon soil texture and environmental conditions. Based on data in soils of different texture in semiarid southwestern Saskatchewan, Canada, Campbell et al. (1996) reported that, over an 11-12 year period, increases in carbon storage in the 0-15 cm soil depth, due to adoption of no-tillage were small and increased with clay content. Most of the differences were observed in the 0-7.5 cm soil depth, with little change in the 7.5-15 cm. Similarly, Novak et al. (1996) reported that organic matter in the surface layer (0-5 cm) of no-tillage soils was approximately twice that of tilled soils after 14 years in the sandy southeastern coastal plain soils. Management effects of organic and conventional farming practice were found to affect total organic carbon as well as light fraction SOM (Wander and Traina, 1996a) in the Rodale farming system trial (Kutztown, USA), which includes a conventional and two organic systems, one based on legumes and another on manure as nutrient input. Hassink et al. (1997), using a combined size-density fractionation technique to differ microbial biomass from size-density fractions between different tillages, demonstrated that the amount of macroorganic matter (> 150 μm) is controlled by soil management, while the amount of carbon associated with clay and silt particles is controlled by soil texture. Frequently, soil organic carbon concentrations increase at the surface of no-tillage soils as a result of plant residue accumulation and erosion abatement. In some cases, decay rates of

residues placed at the soil surface are slow compared to residues that are incorporated. However, surface residues appear to decay rapidly at the surface of soils where moisture and nutrient status are non-limiting. Wander and Yang (2000) found that in the spring after soybean production in a corn soybean rotation, the quantity of residues did not differ significantly among plots that had been under moldboard plowed and no-tillage management for over a decade. Therefore, greater knowledge of the carbon dynamics occurring after tillage is needed to understand and accurately predict its effects on soil organic carbon sequestration. The conservation and conventional tillage experiments at the Pee Dee center was initiated to assess the impact of conservation tillage and residue management on a soil typical of the southeastern Coastal Plain (Novak et al., 1996). However, the changes of SOM quality and their effect on pesticide sorption need further investigation.

Cover crops can play an important role in nutrient management for agricultural regions (Guideau et al., 2001; Willson et al., 2001). Cover crop systems which maintain productivity while reducing nutrient and soil losses will be most acceptable to farmers. The effects of cover crops on soil properties are dependent on rainfall amount and distribution, soil type, cover crop species, and fertilizers. Wander and Traina (1996a) showed that SOM in crop rotation with cover crops was significantly higher than in those rotations without cover crops. However, Lal et al. (1991) in a similar type of study reported no or minimal change of SOM content. This could be due to the complexity of the continuum of organic materials that make up SOM and by the fact that a large proportion of the organic matter in

soil is quite old. Willson et al. (2001) found that microbial biomass was a less reliable indicator of changes in substract availability than either particulate organic matter or nitrogen mineralization potential (the intrinsic ability of the soil to supply inorganic nitrogen through mineralization over time). Based on the study in Southwest, MI over a 2-year period, they further reported microbial biomass was not enhanced by cover crops. They concluded microbial biomass functions as a catalyst for microbial degradation rather than as a long term source or sink of mineralizable nitrogen in their coarse textured soils. By investigation of vegetation control on soil organic dynamics, Quideau et al. (2001) concluded that the global mosaic of vegetation exerts significant influence on the accumulation and turnover of SOM directly by determining the palatability of plant material and indirectly by conditioning the pathways of biomass incorporation into soil. Therefore, more research is needed to clarify the functional relationship and to quantify accessible SOM pools and their implications on soil fertility and plant nutrition. The cover crop experiments at University of Massachusetts (Amherst) research farm (South Deerfield) were conducted to study nitrate-N leaching with varying nitrogen fertilizer rates and with varying vetch seed rates. However, the quantity and quality changes of SOM and pesticide sorption under different cover crop systems need to be addressed.

In the global carbon cycle, SOM is a major source/sink of atmospheric carbon. Thus, in addition to SOM quantity, the quality (*e.g.*, structure and composition) and distribution of individual fractions (*e.g.*, humic acids, polysaccharides) are essential to the maintenance of soil productivity. Preston et al. (1987) reported differences in

composition of organic matter of virgin and cultivated organic soils using solid-state ^{13}C NMR. Cultivated sites had less carbohydrate and more lipid and methoxyl-C than did the virgin sites. Stearman et al. (1989) found that humic acid (HA) differed by soil depth and crop using solution-state ^{13}C NMR. Olk et al. (2000) used Fourier-transform infrared, fluorescence, and electron spin resonance methods to analyze the elemental composition and acidic functional groups of the labile mobile humic acid fraction and the more recalcitrant calcium humate fractions. Soil samples were from four long-term field trials on the International Rice Research Institute farm, which varied in the number of annual irrigated rice crops and hence degree of soil submergence. They reported that, with increasing soil submergence, the HA fractions became less oxidized or humified, with higher sulfur and hydrogen and lower oxygen concentrations, more amide or amino, hydroxyl, and methoxy groups, and fewer carboxyl groups and organic free radicals. All the information above demonstrated the individual fraction of SOM varies with soil management.

Humic substances (HS) are heterogeneous mixtures. The early work (Stevenson, 1994; Hayes, 1997) indicates that the HS from the same soil types and formed under the same environmental conditions are similar. However, there are distinct compositional differences among HS from different sources, soil types, and climates.

The HS are of environmental significance (Stevenson, 1994). They contain a wide variety of functional groups, such as carboxyl (COOH), carbonyl (C=O), and hydroxyl (OH), which can react with metal ions to form complexes (Schnitzer and

Khan, 1972). HS may be involved in transportation of hydrophobic organic compounds (HOC). For instance, sorption is a key process regulating the fate, mobility, and bioavailability of HOC in soils. Sorption reduces the rate of biodegradation and leaching (Pignatello and Xing, 1996) and bioremediation (Alexander, 1995). HS may also be responsible for the enrichment of uranium and other metals in various bioliths such as coal.

The characteristics of HS are fundamental to understanding their roles in nature and environmental protection. Because of the heterogeneous nature of HS, a specific type of functional group may exist in a range of chemical environments, each of which responds somewhat differently to a given measurement probe. Despite inherent difficulties in the study of HS and their exact chemical structure, much information has been gained about their composition in recent years. Swift (1996) has updated the wet chemical and some spectroscopic procedures for determining functional groups in HS. There are comprehensive reviews on acidic functionalities (Perdue, 1985), using various spectroscopic procedures such as infrared (MacCarthy and Rice, 1985), both proton and ^{13}C Nuclear Magnetic Resonance (NMR) (Wilson, 1989), electron spin resonance (ESR) (Senesi and Steelink, 1989), and vibrational, electronic, and high energy spectroscopic methods (Bloom and Leenheer, 1989). Perdue (1985) stressed how the same functional groups can have different pK_a values in different local molecular environments. Niemeyer et al. (1992) provided diffuse reflectance infrared Fourier-transform (DRIFT) spectra of IHSS (International Humic Substances Society) reference HA. Simpson et al. (1997) determined fluorescence spectra for HA isolated in water,

and at pH 7, 10.6, and 12.6 from the Ah horizon of a forest podzol. E_4/E_6 ratios (absorbency at 465/665 nm) can give useful comparisons for humic samples from different sources (Simpson, 1997).

So far, NMR provides the most useful HS compositional information (Wilson, 1987; Preston, 1996). Progress was also made when techniques such as multiple pulse Fourier transform NMR, cross-polarization and magic-angle spinning (CPMAS) NMR were introduced. These techniques enable better functional group assignments and allow a degree of quantification to be achieved.

1.2 Quantitative investigation of HS with solid-state NMR

In order to better understand the dynamic mechanisms of HS with organic and inorganic pollutants, it is absolutely necessary to obtain the structural information of HS (Cameron and Sohn, 1992; Xing et al., 1994a, 1994b; Xing and Pignatello, 1996; Hayes, 1997; Xing and Pignatello, 1997, 1998; Xing, 1998; Xing and Chen, 1999; Mao et al., 2000). Because of the heterogeneous nature of HS, elemental analysis data show only the average of molecular agglomerations, not a precise structure. Analytical pyrolysis techniques have given valuable information on the possible chemical constituents and building blocks of HS (Stevenson, 1994), but the cleaved components may be much different from the molecules that actually compose HS. Many spectroscopic methods such as infrared, electron spin resonance, fluorescence and NMR have been used to study HS components and structure (Simpson et al., 1997). NMR is one of the most widely accepted (Preston, 1996; Nanny et al., 1997). Cross-Polarization Magic-Angle Spinning ^{13}C NMR has been extensively used to study HS structures (Wilson, 1987; Stevenson, 1994; and

Preston, 1996) by using a combination of the following techniques to improve spectral quality. 1). High power proton decoupling: HS contain two interacting spin species ^{13}C and ^{1}H. Much of the C line broadening arises from interactions between the two. Through high power proton decoupling, the magnetic influence of the proton nuclei on a neighboring ^{13}C nuclei is eliminated or minimized, thereby reducing line broadening. 2). Cross-polarization (CP) is the second technique for reducing line broadening. Essentially, this technique results in the transfer of net magnetization from the abundant ^{1}H spins to the less abundant ^{13}C spins. Energy transfer between nuclei with widely differing Larmor frequency can be made to occur when $\gamma_C B_{1C} = \gamma_H B_{1H}$. This equation expresses the Hartmann-Hahn condition. Since γ_H is four times γ_C, the Hartmann-Hahn match occurs when the strength of the applied carbon field B_{1C} is four times the strength of the applied proton field B_{1H}. When the proton and carbon rotating frame energy levels match, polarization is transferred from the abundant protons to the rare ^{13}C nuclei. This procedure also overcomes the problem of dipolar line broadening; in addition, resolution is enhanced by an increase in net ^{13}C magnetization. 3). Magic Angle Spinning: this is a technique for further decreasing line broadening by eliminating the remaining vestiges of dipolar ^{13}C-^{1}H interactions and chemical shift anisotropy effects. By rapidly rotating the sample at the so called "magic angle" with respect to the applied magnetic field, this magic angle is 54.7^{o}.

However, there are several problems with this technique, which can lead to non-quantitative spectra (Alexson, 1985; Wershaw and Mikita, 1987; Wilson, 1987; Schmidt-Rohr and Spiess, 1994; Kinchesh et al., 1995a, 1995b). The first

problem is the reduced cross-polarization (CP) efficiency for unprotonated carbons, mobile components, or regions with short $T_{1\rho}H$ (proton rotating-frame spin lattice relaxation time). CP efficiency relies on the distance between ^{13}C carbons and protons. Thus, ^{13}C carbons without directly bonded protons have a reduced CP efficiency. Molecular mobility, which reduces the dipolar interaction, can also significantly decrease the CP efficiency. The presence of paramagnetic ions is of particular concerns. Since these may assist relaxation and greatly shorten $T_{1\rho}Hs$ in their immediate vicinity. Thus if there is a collection of $T_{1\rho}Hs$ in a mixture, some carbon components will not be quantitatively determined. To obtain quantitative data, spectra at several cross polarization times may have to be obtained to account for variations in $T_{1\rho}Hs$. The next quantification problem arises from spinning sidebands, which reduce the intensity of the centerband, leading to the loss of intensity and distortion of peak areas. The third problem in obtaining reliable spectra is the baseline distortion due to a dead time at the start of the detection. This is particularly serious for HA due to their broad spectral lines and wide dispersion of chemical shifts.

The Total Sideband Suppression (TOSS) pulse sequence could be used to remove spinning sidebands before detection (Dixon et al., 1982). After examining several solid-state ^{13}C NMR techniques, CP-TOSS was recommended to study SOM (Xing et al., 1999). There are two advantages of CP-TOSS over simple CP-MAS. The first is that a good TOSS can eliminate all the sidebands so that the spectrum shows only the true peaks for a HA sample. The second is that implementation of CP-TOSS can avoid baseline distortion arising from the dead

time. Although it is difficult to obtain absolutely quantitative spectra using CP-TOSS, comparisons of different CP-TOSS spectra for samples from similar sources can be made by assuming the same CP efficiencies. Thus, CP-TOSS will be used in this study.

1.3 Characteristics of HS by DRIFT

Transmission infrared (IR) spectroscopy has been widely used for the complex organic macromolecules such as HS (Schnitzer, 1971; Stevenson and Goh, 1971; Stevenson, 1994; Inbar et al., 1989) and coal (Painter et al., 1985). The IR spectra of such macromolecules contain a variety of bands that are diagnostic to their signatures.

The development of high performance FTIR has resulted in improved transmission spectra of HS obtained from various sources (MacCarthy and Rice, 1985; Inbar et al., 1989). The technique and theory of diffuse reflectance Fourier transform infrared spectroscopy (DRIFT) are well documented and reviewed (Fuller and Griffiths, 1978; Painter et al., 1985). The DRIFT spectra can be described by the Kubelka-Munk function (KM) where KM is the ratio of diffuse reflectance from the sample and the diffuse reflectance from a non-absorbing powder. This ratio is related to sample absorptance (a), concentration (c), and a scattering coefficient (s) in the following manner:

$$KM = 2.303ac/s$$

If specular reflectance is small and scattering is constant, then KM should vary linearly with sample concentration. However, because scattering and the actual irradiated concentration of similarly prepared samples do vary, direct quantitative

analysis through application of Beer's law is not possible (Wander and Traina, 1996b). To get around this problem, the relative heights or intensities of selected peaks have been used for comparative analysis of DRIFT spectra (Griffiths and Fuller, 1982).

Niemeyer et al. (1992) demonstrated the utility of the peak ratio technique for semiquantitative analysis of SOM fractions prepared over a range of sample concentrations. They compared IR, FTIR, and DRIFT spectroscopy with regard to their applicability to HA, peat, and compost characteristics and found that DRIFT spectra had higher resolution and the samples were easier to prepare than other spectra. In addition, by using DRIFT, they were able to minimize the interference from water, and the resolution was improved. The possibility of using DRIFT spectra to quantitatively measure sample concentration and to measure the relative concentration of functional groups was assessed. Niemeyer et al. (1992) found that there was no relationship between peak intensity and HA concentration. Therefore, their results indicated that although DRIFT spectroscopy cannot be used to quantify the absolute C contents of structural groups, it can be used to generate peak ratios from which one can assess the reactive enrichment and depletion of specific functional groups within complex organic and organo-mineral spectra. Using a similar approach, Inbar et al. (1989) used DRIFT peak ratios to semiquantitatively assess the maturation of composted manure. They found that, as manure composted, its aliphatic peak constituents were relatively decreased as the proportion of aromatic functional groups increased. Wander and Traina (1996b) used ratios of reactive (O-containing) and recalcitrant (C, H and/or N) functional

group heights to characterize SOM fraction composition. Based on peak ratio comparisons, they determined that HA in the manure-amended organic fraction was more reactive than HA isolated from crop-residue-amended soils. Reactive/recalcitrant (O/R) peak ratios indicated that the FA and particulate organic matter (or light fraction, LF) they isolated were most reactive in the organic cash-grain-based rotation. No consistent link between SOM fraction O/R ratios and reported C/N ratios or biological availability was made. The peak ratio technique allows DRIFT spectra to be used to semiquantitatively assess the functional group composition of a wide range of SOM fractions.

It is expected that the application of DRIFT to organic matter research will prove to be a useful tool for characterizing bulk heterogeneous samples such as humic materials, peats and composts. The sample preparation and recording conditions for DRIFT analysis are given by Niemeyer et al. (1992) and Wander and Traina (1996b). Peak assignments and ratio calculation will be done following the method of Wander and Traina (1996b).

1.4 Sorption dynamics study of hydrophobic organic pollutants in SOM

Sorption is a general term for uptake of a solute by SOM without the implication of specific mechanisms. Adsorption refers to condensation of solutes on surfaces or interior pores of SOM; Partition refers to uptake of a solute into the three-dimensional SOM network (Neilson, 1994). The mechanisms for sorption of HOCs (hydrophobic organic compounds) in SOM have been a subject of debate in the literature for many years, and no consensus on sorption mechanisms has been reached to date. The partition model (Chiou, 1989, and references therein) has

become well enriched in the literature, for instance in the widely used textbook "Environmental Organic Chemistry" (Schwarzenbach et al., 1993) and "Environmental Soil Chemistry" (Sparks, 1995). This partition model has also been used extensively in fate and transport models.

Despite the large number of studies supporting linear sorption of HOCs to SOM, many recent investigations have shown nonlinear isotherms, competitive effects in multi-solute systems (Xing and Pignatello, 1996, 1998; Yuan and Xing, 1999; Carmo et al., 2000), and concentration-dependent enthalpy of sorption (Yuan and Xing, 1999). Those observations cannot be explained by the partitioning model and have been attributed to dual mode sorption properties to SOM (Pignatello, 1998; Chen et al., 2000; Pignatello, 2000).

Xing and Pignatello (Xing and Pignatello, 1996, 1997, 1998) proposed SOM as a dual-mode sorbent, in which both solid-phase dissolution and hole (site)-filling mechanisms take place and in which competition takes place only in the hole-filling domain. The hole-filling domain is postulated to be the condensed parts in SOM. In this model, these holes are thought to be nonuniform in size and energy and as a result, discriminate on the basis of molecular structure.

The dual-mode mechanism was first introduced to describe the combined rubbery and glassy state sorption behavior of chemically heterogeneous polymers (Vieth and Slodek, 1965). Polymers can be classified as rubbery or glassy on the basis of internal polymer segment motion, void space, and cohesive forces. Rubbery polymers have a relatively expanded, flexible structure, while glassy polymers have a more rigid, condensed structure. Sorption in rubbery polymers

obeys Henry's law and is noncompetitive; while sorption in glassy polymers is nonlinear and competitive. It was suggested that Langmuir sites postulated to be unrelaxed free volume "microvoids" exist in rigid regions of the glassy polymer matrix. SOM sorption behavior has been likened to that of glassy polymers by recent investigators (Weber and Huang, 1996; Xing and Pignatello, 1996, 1997, 1998). Using X-ray diffraction (XRD) techniques, several researchers have reported the presence of condensed aromatic and expanded aliphatic regions in humic substances from different sources (Schnitzer et al., 1991; Xing and Chen, 1999).

The use of NMR for sorption studies can provide three types of data (Nanny et al., 1997): changes in chemical shift positions, line broadening changes, and changes in the spin-lattice relaxation time (T_1). These are all functions of the media surrounding the sorbate. Therefore, any changes due to associations through partitioning or adsorption will cause a change in the NMR spectrum by changing one or more of these parameters. By detecting sorbed hydrocarbons in a porous medium using proton NMR, Daughney et al. (2000) reported that in the absence of paramagnetic iron impurities, T_1 (relaxation time of proton) remains constant in the presence of sorbed hydrocarbons. T_1 increases with increasing hydrocarbon concentration only if the silica surface is coated with a paramagnetic substances such as iron oxyhydroxide. These results suggest that increases in T_1 previously observed for water in natural materials coated with oil are caused by the shielding of paramagnetic surface sites by the sorbed hydrocarbons. Kohl et al. (2000) used solid-state ^{19}F NMR to investigate hexafluorobenzene (HFB) sorption to SOM and

reported that the uptake of HFB by two peat samples gives direct spectroscopic evidence for the existence of dual-mode sorption to SOM. For example, after 17 minutes of incubation there are sharp peaks at –163.2, -167.0, and –167.4 ppm. The prominent –163.2 ppm peak at 17 minutes decreases with time until after 4 hours when it is almost gone. This rapid decrease is attributed to free, liquid HFB which has not been sorbed into the SOM (the chemical shift of neat HFB was observed to be –163.0 ppm). The peaks at –167.0 and –167.4 ppm (they are attributed to loosely bound, mobile HFB) increase rapidly between 17 and 25 minutes and continue to slowly increase up to 4 hours, after which they only increase slightly with increasing incubation times. Thus, the sorption process is shown to be rapid, with all applied HFB sorbed within a few hours. Extractable lipids compete for high energy sorption sites in the organic matter, and their removal increases the amount of rigidly sorbed, immobile species formed. Solid lipids enhance the sorption capacity of the solid state dissolution domain of the organic matter. This dissolution domain is responsible for partitioning in the dual mode phenomenon. Removal of the lipids decreases the partitioning capacity of the SOM. Nanny (1999) demonstrated that deuterium ^{2}H NMR T_1 relaxation time measurements can be used to examine noncovalent interactions between monoaromatic compounds and fulvic acid (FA). The nature and strength of the noncovalent interactions mostly are a function of the polarity of the monoaromatic compounds and solution pH, as well as the identity and concentration of the FA. Monoaromatic molecules that are proton-donors, such as phenol, appear to form strong noncovalent interactions more preferentially with water than with FA.

The SOM is the principal sorbent, particularly for hydrophobic organic compounds (HOC) in water-saturated systems (Chiou, 1989). Sorption increases with elevated levels of SOM and may reduce leaching potential (Novak et al., 1996). The quality (composition and structure) of SOM also influences sorption. Nanny and Maza (2001) reported that the percent aromaticity of the HA and FA and the solution pH influences the extent of noncovalent interactions with monoaromatic compounds. For example, benzene interacts with dissolved HA at all pH values; however, these interactions increase with decreasing pH and generally are proportional with the HA percent aromaticity. Pyridine behaves similarly to benzene; however, two modes of interaction between pyridine and HA were detected as a function of pH and HA type. Sorption of hydrophobic compounds to SOM has been shown to be directly related to the percent aromaticity and inversely related to the SOM polarity. Organic matter with high aromaticity sorbs more aromatic compounds such as benzene and xylene (Xing et al., 1994; Xing, 1997). Furthermore, sorption of benzene, xylene, and naphthalene is inversely related to polarity of SOM expressed as a mass ratio of (N + O)/C (Xing, 1997). Sorption of dichlorobenzenes is apparently higher in humin fractions than HA, especially at low concentrations (Xing and Pignatello, 1997). Celis et al. (1997) also reported that sorption of atrazine and simazine is higher on Fluka HA than on soil HA, even though the organic C contents of the two HAs are nearly the same. The difference in the sorption of these two pesticides may be attributed to the structural differences (e.g., aromaticity) of the two HAs. However, after studying pyrene sorption by natural organic matter, Chefetz et al. (2000) reported that the aliphatic C-containing

groups is at least as important as aromatic structures in binding of pyrene and possibly other PAHs (polycyclic aromatic hydrocarbons). For example, cuticle and humin samples, which are composed of predominantly aliphatic C, exhibited the highest pyrene K_{oc} (distribution coefficient) values. However, the aliphatic structures do not act alone in pyrene sorption. The degraded lignin sample, which has very little paraffinic C-containing groups, also exhibited high pyrene K_{oc} values. As discussed above, there is presently no agreement about the effect of the nature of SOM on sorption of HOC. It is evident that the effect of structural differences of SOM on pesticide sorption requires further scientific investigations to better understand pesticide efficacy and fate in soils, and to minimize pesticide use and leaching. Whole soil and SOM fractions (HA, humin fraction) will be used. Based on soil organic carbon content and spectroscopic analysis, we will use samples from representative plots for sorption and desorption experiments. The batch equilibrium method will be used for this study.

1.5 Objectives

SOM is an important indicator of soil quality and sustainable agriculture because it can improve physical, chemical, and biological properties of soils and nutrient supplies. SOM also affects pesticide sorption, mobility, use, and efficacy. However, the effect of agricultural practices on SOM, particularly structural and compositional changes, and the relationship between SOM changes and soil and environmental quality are unclear. As a result, it is difficult to evaluate the effectiveness of agricultural options to maintain or improve soil and environmental quality. A better understanding of SOM changes and their impacts on pesticide

sorption/desorption as affected by agricultural practices is essential to sustainable agriculture.

The present research addresses chemistry and characteristics of SOM in long-term tillage and cover crop systems. The soils used for the research represent typical agricultural soils in the Connecticut River Valley (the Northeast) and the Southeastern Coastal Plain. In addition, this research addresses sorption behavior and mechanisms of pesticides in soil and their relationship with SOM characteristics. Interactions between hydrophobic (nonionic) organic contaminants (NOC) and natural organic matter strongly influences the fate and transport of NOC in the environment. Characterization of the chemical interaction between NOC and organic matter can potentially provide information on important aspects of the sorption mechanisms. This information may be useful to explain the influence of organic matter characteristics on NOC sorption and the mechanisms controlling nonequilibrium sorption of NOC to organic matter.

Based on the information above, the specific objectives are: 1. to examine quantitative, structural and compositional changes of SOM and its individual fractions (e.g., light fractions) as affected by agricultural practices; 2. to determine the sorption dynamics and mechanisms of metolachlor in SOM and soil under different soil managements.

CHAPTER 2

SOIL ORGANIC MATTER CHARACTERISTICS AS AFFECTED BY TILLAGE MANAGEMENT

2.1 Abstract

Soil organic matter (SOM) is of primary importance for maintaining soil productivity, and agricultural management practices may significantly influence SOM chemical properties. However, how SOM chemical characteristics change with agricultural practices is poorly understood. Therefore, in this study, we evaluated the impacts of tillage (conventional vs. conservation) management on the structural and compositional characteristics of SOM using Cross-Polarization Magic-Angle-Spinning (CPMAS) and Total Sideband Suppression (TOSS) solid-state ^{13}C Nuclear Magnetic Resonance (NMR) and Diffuse Reflectance Fourier Transform Infrared (DRIFT) spectroscopy. We characterized both physically and chemically isolated SOM fractions from a Norfolk soil under long term tillage management (20 years). The solid-state ^{13}C NMR results indicated that humic acid (HA) from conventional tillage (CT, 0-5 cm) was less aliphatic and more aromatic than HA from conservation tillage (CnT). The aliphatic carbon content decreased with increasing depth (0-15 cm) for both CT and CnT treatments. The reverse trend was true for aromatic carbon content. Based on reactive/recalcitrant (O/R) peak ratio comparisons, HA was more reactive in the top soil (0-5 cm) under CnT than CT. Both soil organic carbon (SOC) and light fraction (LF) material were higher in the 0-5 cm soil of CnT than CT treatment. Our results show that long-term tillage management can significantly change the characteristics of both physical and chemical fractions of SOM.

2.2 Introduction

Soil organic matter (SOM) strongly affects soil properties such as water infiltration rate, erodibility, water holding capacity, nutrient cycling and pesticide adsorption (Stevenson, 1994; Campbell et al., 1996; Francioso et al., 2000; Wander and Yang, 2000). It has been suggested that proper management of SOM is the heart of sustainable agriculture (Weil, 1992). Recent research has also recognized SOM as a central indicator of soil quality and health (Soil and Water Conservation Society, 1995). For example, a decline in SOM (biological oxidation and/or erosion) significantly reduced the nitrogen supply and resulted in a deterioration of soil physical conditions, leading to crop yield reduction (Greer et al., 1996). Therefore, it is important to maintain proper levels of SOM to sustain soil productivity.

Intensive agricultural practices change SOM characteristics greatly, generally a substantial loss of soil organic carbon (SOC). Soils of the Southeastern United States, particularly sandy Coastal Plain soils, have inherently low SOC contents (typically below 1%, Hunt et al., 1982). Consequently, small changes in the SOM content are significant to the agricultural production of the region. An evaluation of tillage and crop residue management practices to rebuild SOC levels has been conducted by Hunt et al. (1996). These researchers monitored changes in SOC levels in numerous small tillage plots and found that after 9 years of CnT, the SOC content in the top few cm was significantly higher than the soil under CT management. Campbell et al. (1999) reported that over an 11-12 year period, increases in carbon storage in the 0-15 cm soil depth, due to adoption of no-tillage,

were small (0-3 t ha^{-1}). Most of the differences were observed in the 0-7.5 cm soil depth, with little change in the 7.5-15 cm. However, the short and long-term influences of disturbance on carbon mineralization are complex and may vary depending on types of soil and plant residues (Hu et al., 1995; Franzleubbers and Arshad, 1996; Alvarez et al., 1998). The strong influence of soil management on the amount and quality of SOM was also reported by others (Janzen et al., 1992; Ismail et al., 1994; Campbell et al., 1996).

Another approach to evaluate the impact of agricultural management on SOM dynamics is to separate SOM into pools based on differences in decomposition rates (Wander et al., 1994; Wander and Traina, 1996a). Generally, those pools are conceptualized with one small pool having a relatively quick decomposition rate (i.e., active pool-light fraction, LF) and pools that are more recalcitrant (i.e., humus) (Stevenson, 1994). The LF is sensitive to environmental and agricultural management factors and can be used as a functional description of organic materials (Wander and Traina, 1996a). Regardless of active or recalcitrant SOM pools, structural chemistry is important for their chemical and biological activities.

Spectroscopic techniques can provide useful structural information on SOM. Diffuse reflectance Fourier transform infrared (DRIFT) spectroscopy is considered to be one of the most sensitive IR techniques for humic substances analysis (Niemeyer et al., 1992; Ding et al., 2000). According to Painter et al. (1985) and Niemeyer et al. (1992). This technique offers several advantages over transmission IR spectroscopy: (1) a simple sample-preparation procedure; (2) insensitivity to water associated with the sample and enhanced resolution; (3) high resolution of

the spectra due to reduction in the sensitivity towards light scattering; and (4) a more reliable method for quantitative estimations of functional groups. Another spectroscopic technique is solid-state ^{13}C NMR spectroscopy that is probably the most useful tool for nondestructive characterization of SOM and its components (Preston, 1996; Xing and Chen, 1999; Mao et al., 2000). Studies by Capriel (1997) and Ding et al. (2001b) demonstrate that both DRIFT and ^{13}C NMR techniques are useful and suitable for examining the effects of agricultural management on SOM.

The goal of this research was to evaluate the changes of SOM quantity and quality under CT and CnT systems using both DRIFT and solid-state ^{13}C NMR. Spectroscopic investigations of SOM changes for the Norfolk soil, located in the Southeastern Coastal Plain, have never been conducted before. Furthermore, because organic, sustainable agricultural systems depend increasingly on soil nutrient cycling mechanisms, it is necessary to understand the relationships between the LF, the structural and compositional changes of HA, and nutrient retention and supply characteristics. The specific objectives were to: (i) characterize HA structural changes; (ii) determine peak height O/R (reactive/recalcitrant) ratio for HA, which reflects the biological activity; and (iii) compare the light fraction (LF) variations with soil depth under both CnT and CT systems.

2.3 Materials and Methods

Site Description and Sampling

The study was conducted using soil samples collected from the long-term CnT and CT research plots established in 1979 at the Clemson University Pee Dee

Research and Education Center (Darlington, SC). The soil at the research site is a Norfolk loamy sand (fine-loamy, siliceous, thermic Typic Kandiudult). The coordinates are latitude 34.3° and longitude 79.7°, and the elevation is 37 m above the mean sea level. Treatments were arrayed in a randomized complete block design with split plots and five replications (Hunt et al., 1996).

The CT treatment within the plots consisted of multiple disking (0 to 15 cm deep) and the use of field cultivators to maintain a relatively weed free surface. Surface disking and field cultivation have been completely eliminated in soil under CnT plots since 1979. Because of a root-restrictive E horizon which reforms annually in this soil (Busscher and Sojka, 1987), both tillage treatments received in-row subsoiling (30 cm deep) at planting to fracture this horizon. Additional management practices for the plots such as crop rotation, fertilization, and pesticide application were described previously (Hunt et al., 1996; Novak et al., 1996). In 1999, approximately 50 soil cores were collected from the top 15 cm of soil using a 2.5 cm diameter soil probe at random locations from one plot under CnT and one plot under CT treatment. The core samples were sectioned (5 cm increments), composited, air-dried, and sieved (2 mm).

Density Gradient Separation of LF Material and Analysis

The LF has been recognized to be an important soil nutrient reservoir and has been recommended as a fertility index (Wander et al., 1994). In this investigation, the LF material from each soil layer was isolated using a modified density gradient method of Wander and Traina (1996a). The LF was collected by dispersion of 50 g soil of freshly sieved, field-moist soil sample in a NaBr solution (density 1.5 g/ml,

1:1 w/v). The mixture was shaken for 30 min and centrifuged at 8000 rpm for 20 min. These rinses were then transferred into a 250 ml separatory funnel and allowed to settle overnight. After three such separations, the composite supernatant was filtered using a 0.45 μm polycarbonate membrane filter. The heavy SOM fraction which settled to the bottom of the funnel was removed. The LF materials retained on the filter were rinsed with a 0.5 M $CaCl_2$ and 0.5 M $MgCl_2$ solution followed by a final rinse in deionized water. This was done to avoid any remnant biological toxicity due to Na^+ saturation of the ion-exchange sites in the LF. The weight yield of LF was measured and the light fraction-organic carbon (LF-OC) and total combustible nitrogen content were determined using a LECO-CN 2000 analyzer.

Extraction, Fractionation and Purification of HA and Elemental Composition Analysis

Most of extraction techniques require the organic matter (OC) to be removed from soil (Stevenson, 1994). As a consequence, the OC constituents would be modified to some extent. Therefore, we used neutral pyrophosphate ($Na_4P_2O_7$) to extract SOM to minimize chemical modifications (Stevenson, 1994). Air-dry and sieved soil (50 g) was weighed into a 1000 ml plastic bottle, and 500 ml 0.1 M $Na_4P_2O_7$ were added. The air in the bottle and solution was displaced by nitrogen gas (N_2) and the system was shaken for 24 hours at room temperature. The samples were extracted three times. After separation from the $Na_4P_2O_7$ insoluble residues by centrifuging at 3000 rpm, the dark-colored supernatant solutions were combined, acidified to pH 1 with 6 M HC1, and allowed to stand for 24 hours at room

temperature for the precipitation of the HA fraction. The HA was shaken for 24 hours at room temperature with 0.1 M HCl/0.3 M HF solution at least for 3 times. The insoluble residues (HA) was separated from the supernatant by centrifuging at 10000 rpm, washed with deionized water until free of chloride ions, and then freeze-dried. The C, H, and N contents of the isolated HAs were measured with a Fisons Model EA 1108 Elemental Analyzer.

DRIFT Analysis

The DRIFT spectra were collected using an Infrared Spectrophotometer (Midac series M 2010) with a DRIFT accessory (Spectros Instruments). All HA fractions were powdered with a agate and pestle and stored over P_2O_5 in a drying box. Three mg solid HA samples were then mixed with KBr (total weight as to 100 mg) and reground to powder consistency. A sample holder was filled with the mixture (powder). A microscope glass slide was used to smooth the sample surface. At the beginning of analysis, the diffuse-reflectance cell which contained the samples was flushed with nitrogen gas for 10 minutes to reduce the interference from carbon dioxide and water molecules. The sample compartment was placed with anhydrous $Mg(ClO_4)_2$ to further reduce atmospheric moisture.

The DRIFT spectroscopy was acquired with a minimum of 100 scans collected at a resolution of 16 cm^{-1}. The spectroscopy was calibrated with the background which consisted of powdered KBr and scanned under the same environmental conditions as the sample-KBr mixtures. Absorption spectra were converted to a Kubelka-Munk function using Grams/32 software package (Galactic Corporation). Peak assignments and intensity (by height) ratio calculation were

done following the methods of Niemeyer et al. (1992), and Wander and Traina (1996b). We used ratios of labile (O-containing) and recalcitrant (C and H and/or N) functional groups to compare HA spectra with varying soil depth of different tillage treatments.

Solid-State ^{13}C NMR Spectroscopy

Spectra were obtained by using the CPMAS-TOSS techniques. Xing et al. (1999), after examining several solid-state ^{13}C NMR techniques including ramped CPMAS, reported that CPMAS-TOSS has two advantages. The first is that an adequate TOSS can eliminate the sidebands so that the spectrum shows only the true peaks for a given HA sample. The second is that implementation of CP-TOSS can avoid baseline distortion from the dead time. In addition, instrument time required is about the same as the regular CPMAS. They recommended that CPMAS-TOSS be used to analyze HA samples when using a ≥300 MHz spectrometer. In this research, HA samples were run at 75 MHz (^{13}C) in a Bruker MSL-300 spectrometer with a 7-mm CPMAS probe. The samples (300-350 mg) were packed in a 7-mm-diameter zirconia rotor with a Kel-F cap. The spinning speed was 4.5 kHz. A ^{1}H 90° pulse was followed by a contact time (t_{cp}) of 500 μs, and then a TOSS sequence was used to remove sidebands (Schmidt-Rohr and Spiess, 1994; Xing et al., 1999). Line broadening of 30 Hz was used. The 90° pulse length was 3.4 μs and the 180° pulse was 6.4 μs. The recycle delay was 1 s with the number of scans about 4096. The details were reported elsewhere (Xing et al., 1999). In preliminary experiments, we ran several samples at different contact times, and selected 500 μs because this contact time gave the best signal to noise

ratio and the spectra were similar to the ones generated by direct polarization MAS ^{13}C NMR. There was no signal observed for the rotor and Kel-F cap (Mao et al., 2000), thus, no background correction was made in this work.

Statistical Analyses

All data presented were the mean of at least three replicate measurements, except for HA elemental composition and solid-state ^{13}C NMR data because of the high cost and low availability of the instrument. However, preliminary solid-state NMR experiment with one HA sample indicated minimal variations, which was consistent with the result of an extensive NMR study in our lab (Mao et al., 2000). The HA elemental composition and NMR measurements were performed on composite samples.

The fraction of total SOC and total combustible nitrogen (TCN) pools in the unfractionated soil and in LF was compared using a two-way Analyses of Variance (ANOVA). Also, the O/R ratios generated from DRIFT peak heights were examined between tillages and by depth using the ANOVA. Different tillage treatments and soil depths were the experimental factors and the interactions between tillage and depth were examined. SigmaStat software (SPSS Corp., Richmond, CA) was used for each test at a 0.05 level of significance.

2.4 Results

Yields of LF Material and Elemental Composition of HA

The total quantities of SOC, TCN and LF found in soils calculated from bulk density under CnT and CT management are shown in Table 2.1. It is clear that twenty-year different tillage management influenced the quantity and distribution

of C, LF and N in the soil. Twenty year CnT treatment resulted in a significant increase in the SOC, soil-TCN, and LF in the top 0-5 cm soil layer of the unfractionated soil, as compared with CT management. The quantities of SOC, TCN and LF in the 0-10 cm layer were significantly higher than those of 10-15 cm depth under CT treatment. The SOC and TCN decreased with increasing soil depth under both tillage treatments.

The quantity of LF material in the 0 to 5 cm soil layer in the CnT system was approximately twice high as that in the CT system. On the other hand, soil under CT management at the 5 to 10 cm layer had significantly higher LF than soil under CnT. The dependency of tillage and depth on LF distribution was confirmed by the two-way ANOVA which showed that there was a significant tillage and depth interaction ($P < 0.01$) when the quantity of LF was compared between tillages. Additionally, regression analyses between the quantity of LF material and the quantity of SOC showed a significant linear relationship (r^2 between 0.89 to 0.97, $P \leq 0.01$) (data not shown). This relationship indicates that 89 to 97% of the variation in quantity of LF material isolated from soil under both tillages can be accounted for by the SOC content.

The isolated LF material accounted for between 4 to 16% of the total SOC and 2 to 10% of soil TCN from the Norfolk soil (Table 1). Only at the 5 to 10 cm soil depth was there a significant difference of LF-OC and LF-N percentages between tillages. Regression analyses confirmed a significant relationship (r^2 between 0.79 to 0.95) between the LF-OC vs. the SOC content and the LF-TCN vs. the soil TCN

content. The soil C/N ratio for both tillages increased slightly with soil depth, but not significantly (Table 2.1).

The elemental compositions of the HAs from both CnT and CT systems are displayed in Table 2.2. Examination of the data showed that the HAs from two tillage systems were similar to each other. The C content of HA under CnT was slightly lower in the middle layer (5-10 cm) than that of other two layers. The N content was higher in the top soil than that of deeper layers for both tillages. The HA atomic C/N ratio increased with soil depth for both tillages, similar to the soil C/N ratio changes. The HA H/C ratio of CnT plot slightly declined with depth while this ratio was almost constant for CT soil.

Solid-State ^{13}C NMR Spectroscopy of HA

The HA ^{13}C CPMAS-TOSS NMR spectra of both CT and CnT are shown in Figure 2.1. The HA spectra revealed generic chemical characteristics of the components present in the samples. Unsubstituted aliphatic C is indicated by signals in the 0 to 50 ppm region. Carbons in proteinaceous materials (amino acids, peptides, and proteins) have resonances between 40 and 60 ppm, and C in carbohydrates gives signals between 60 to 108 ppm. Signals between 108 to 162 ppm are due to aromatic C, while those near 155 ppm arise from phenolic C, indicating the presence of O- and N-substituted aromatic groups (e.g., phenolic OH and aromatic NH_2). The strong signals between 170 and 180 ppm come from C in carboxyl groups, with possibly some overlapping from phenolic, amide, and ester carbons (Stevenson, 1994; Mao et al., 2000).

It was difficult to directly compare the HA spectra of different treatments because visual comparison showed no major differences in terms of presence or absence of specific peaks. However, we can obtain detailed information from these spectra by peak area integration. The relative content of major C-types, calculated by integrating the spectral profile according to standard chemical shift ranges (Xing et al., 1999) is shown in Figure 2.2. The most noticeable feature was at 60-96 ppm region (Fig. 2.1, Fig. 2.2B), i.e., carbohydrate-C (aliphatic C bonded to OH groups, ether oxygens, or occurring in saturated five or six-membered rings bonded to oxygens). This carbon content for CnT in the top soil (0-5 cm) was 23.9%, and was 18.3% for CT (Fig. 2.3B). The difference between the two treatments can be attributed to the accumulation of carbohydrate materials from fresh residue input in the top soil of CnT treatment. The reverse trend was true in the 10 to 15 cm layer, which showed carbohydrate-C content was higher in CT than that of CnT system. There was not much difference in the 5 to 10 cm layer between both tillages. The lowest carbohydrate-C for both tillage managements occurred at 10 to 15 cm soil layer. The carbohydrate-C decreased with soil depth for CnT. But for CT management, the carbohydrate-C content was almost the same in the first two layers.

The total aliphatic-C (0-108 ppm) of HA for CT treatment (Fig. 2.2A) decreased from 52.5% in the top soil (0-5 cm) to 40.1% at the depth of 10-15 cm. Similarly, the aliphatic-C of HA for CnT treatment decreased from 58.8% in the top soil (0-5 cm) to 40.8% at the depth of 10-15 cm. Furthermore, when comparing the total aliphatic-C (0-108 ppm) and carbohydrate-C (60-96 ppm) of HA between

the two treatments (Fig. 2.2A and 2.2B), it was evident that both aliphatic-C and carbohydrate-C were higher in the top (0-5 cm) soil of CnT than CT. The HA alkyl-C content (0-50 ppm, data not shown) at the 10-15 cm layer was higher in CnT than CT.

Another interesting feature was revealed by the 108-162 ppm of NMR spectra and their integration results (Figs. 2.1A and 2.1B, Fig. 2.2C). The two most pronounced peaks in this region were recorded at about 131 ppm (ring carbons in which the ring is not substituted by strong electron donors such as oxygen and nitrogen) and at 155 ppm (phenols and aromatic amines). Aromatic C (31.7%) in the 0-5 cm layer under CT was higher than that (28.1%) of CnT treatment (Fig. 2.2C). Similarly, HA aromatic-C content in 5 to 10 cm of CT system was greater than that of CnT plot. However, the aromatic-C content was almost the same in the 10 to 15 cm for both tillages, even though aromatic C in both treatments increased with soil depth. The aromaticity (expressed in terms of aromatic C as a percentage of the aliphatic C + aromatic C, according to Hatcher et al., 1981) increased from 32.3% in the top soil of CnT to 50.7% at the 10-15 cm layer, and from 31.7% to 50.8% for CT treatment (Fig. 2D). Carboxyl groups were relatively enriched in CT treatment (data not shown). The value of carboxyl-C increased with soil depth for both treatments, which was consistent with the report by Stearman et al. (1989). Carbonyl-C content was very low (Fig. 2.1) and we did not observe any distribution pattern and change between tillage treatments. This may be due to the poorly resolved carbonyl-C peaks (Fig. 2.1).

DRIFT Spectroscopy of HA

The spectra of HA from CT and CnT are presented in Figure 2.3. The resolution of the spectra exhibited a significant improvement, compared with previously published spectra obtained using dispersive or FTIR spectrophotometers. Evidence for the presence of COOH groups was indicated by the peak at around 1700-1720 cm^{-1}, which was attributed to C-O stretch and OH deformation of COOH groups. The band around 1620-1600 cm^{-1} in all of the HA spectra was assigned to aromatic C=C and the asymmetric C=O stretching in COO^- groups (Inbar et al., 1989; Gressel et al., 1995). But the frequency at 1660 cm^{-1} can also be attributed to internal hydrogen bonds of carbonyl groups (Bellamy, 1975). Peaks around 1400 cm^{-1} were assigned to CH_2 and CH_3 bending, C-OH deformation of COOH, and COO^- symmetric stretch (Celi et al., 1997). The bands in the 1100 to 900 cm^{-1} region were usually attributed to polysaccharide and silicate vibrations (Francioso et al., 2000). The peak around 600 cm^{-1} of HA was associated with unknown mineral compounds (e.g., silicate, oxides, and/or organo-mineral fractions).

All DRIFT spectra of HA samples from CnT and CT systems were similar in their basic peak assignments. However, in order to get a clear picture of tillage impacts on spectral composition of HA, we examined ratios of reactive (O-containing) and recalcitrant (C, H and/or N) functional group peak heights (Table 2.3). Based on peak ratio comparisons, the total O/R ratio (R_1) of HA was the highest at 0-5 cm of CnT system, which was significantly greater than that of CT system. The lowest O/R ratio appeared at the depth of 10-15 cm of CT treatment (Table 2.3). With increasing depth, the O/R ratio declined for both tillages (Table

2.3). There were relatively little changes of R_1 between 5 to 10 cm and 10 to 15 cm layers for both tillage systems. The ratio of ketonic and carboxyl (1727 cm^{-1}) groups divided by CH and aromatic peak heights (1457 + 1420 + 779 cm^{-1}) (R_2) was also the highest in the top soil (0-5 cm) of CnT system (Table 3), suggesting relatively enrichment of oxygen associated C (e.g., carbohydrates) over time in CnT plots as compared with CT. However, there were no significant differences of R_2 between soil depth for both tillages (Table 2.3).

2.5 Discussion

Evaluating the effects of tillage on SOM dynamics has been shown to take almost 10 years of experiment before any significant change (Hunt et al., 1996). It has been proposed that the LF be examined because it has been correlated with several procedurally defined soil fractions (e.g., biological pools). The LF may act as an indicator of organic matter status in soil (Wander and Traina, 1996a). Thus, characterizing the size of this fraction, as well as its C and N contents, may show short-term changes due to management practices, which may not be detected when measuring whole SOM pool.

In both tillages, the quantities of LF materials, LF-OC and LF-TCN were highly dependent on the SOC and soil-TCN contents. The CnT had higher yield of LF material in the top soil (0-5 cm) while CT soil had a higher amount of LF material in the 5 to 10 cm layer. The findings support the conclusions of Novak et al. (1996) that long-term CnT management creates a SOC-enriched surface zone. Conversely, SOC contents in the CT managements were fairly similar between soil layers probably as a result of mixing by disking. However, for assessing the effects

of tillage and fallow frequency on soil quality, Campbell et al. (1999) reported that total organic C and N were surprisingly superior to the more labile attributes (e.g., microbial biomass). They had anticipated a significant influence of tillage on soil quality attributes, especially the labile ones, but they failed to obtain the expected results. This is probably due to the difference in soil texture and environmental conditions. They used a silty loam (Typic Haploboroll) in a cool-semiarid region (Saskatchewan, Canada), in comparison with a Norfolk loamy sand soil in a warm-humid region (SC, USA) in our study.

Because HA is probably the largest single SOM pool in mineral soils, which is representative of the stage of humification, decomposition pathways have been studied most extensively using HAs (Guggenberger et al., 1994; Preston et al., 1994; Preston, 1996). Microbial decomposition of plant residue has a large influence on the elemental composition of SOM pool. In general, the compounds with narrow C/N ratios are in a more advanced stage of decomposition (Yakovchenko et al., 1998). However, this was not the case for our HAs. The C/N ratio of HA ranged from 15.7 to 20.3 (for comparison, 10.4 to 13.5 for soil) (Tables 2.1 and 2.2) and increased with soil depth for both tillages. This result suggests that some nitrogen-containing compounds of SOM, particularly in the deeper soil layers, may be protected by physical encapsulation in 3-dimensional structures with soil minerals, which were resistant to chemical extraction. Thus, nitrogen contents in the $Na_4P_2O_7$ extracted HA were relatively low (i.e., high C/N ratio). This finding was consistent with the reports of Knicker and Hatcher (1997), and Zang et al. (2000). By changing the conformational structure of HA, Zang et al. (2000) created

new refractory organic nitrogen in HA. The newly formed proteinaceous materials in HA were physically encapsulated within the HA structure. They concluded that physical protection is one of the important factors accounting for the preservation of organic nitrogen in soils and sediments.

Examination of CPMAS-TOSS ^{13}C NMR data illustrated very interesting information. Compared with CT system, HA in the top soil (0-5 cm) of CnT had a higher proportion of carbohydrate-C (Fig. 2.2B). The trends observed were consistent with enhanced decomposition of plant inputs in the CT plot. This was supported by the relatively higher O/R ratio (R_1) of HA in the top (0-5 cm) soil under CnT management. The high O/R ratio indicated that SOM was more biological active. From this study, one may conclude that DRIFT and NMR can be used as complementary methods for the characterization of humic substances. This result also concurred with the LF data that CnT had a significantly higher LF material in the 0 to 5 cm of soil than that of CT plot, indicating that twenty years of CnT management changed structures and compositions of SOM. Our results were in agreement with the observation that numbers of microbes, microbial biomass and potentially-mineralizable nitrogen were greater for no-tillage than CT in the 0 to 7.5 cm soil depth (Doran, 1980). These changes can be sufficient to differences in the available soil water content between tillages (Hunt et al., 1996).

Our observation of a substantial increase of aromatic-C in HAs with soil depth for both treatments implied that the humification processes were more advanced in deeper soil layers. This result was in good agreement with the report of Preston (1996) that as the aromatic rings of lignin are modified, a single broad peak with its

maximum around 131 ppm starts to dominate in the aromatic region. With further humification, HAs may become highly aromatic, with development of polycondensed rings (Chen and Pawluk, 1995; Preston, 1996; Xing and Chen, 1999). Reduction of H/C ratio of HA in CnT plot (Table 2.2) with soil depth supported the increased aromaticity (Fig. 2.2D) as observed by NMR. However, this was not the case for the CT plot as H/C ratio was almost the same for all soil depths. The reason was unknown.

From the data of LF, and NMR and DRIFT results of HA, the SOM in the top soil layer (0-5 cm) of CT plots seems more chemically and physically stable than CnT. This is consistent with the results of Stearman et al. (1989), Wander et al. (1994) and Wander and Traina (1996) that the CT soil had a greater proportion of all SOM in the more stable fraction. From a more practical point of view, CnT managements can not only maintain the levels of SOC, but also substantially improve soil quality as reflected by reactive HA and high content of LF materials.

From the discussion above, it is clear that the tillage treatments have changed the chemical composition and structure of SOM. This can potentially affect pesticide fate and efficacy in soil. Nanny and Maza (2001) reported that the HA aromaticity and the solution pH influenced noncovalent interactions between HA and monoaromatic compounds. Celis et al. (1997) also reported that sorption of atrazine and simazine was higher on Fluka HA than on soil HA, even though the organic C contents of the two HAs were nearly the same. Moreover, sorption of organic compounds was positively correlated with aromaticity and negatively with polarity of SOM (Xing et al., 1994a,b,c; Xing, 1997; Ahmad et al., 2001). Sorption

of several pesticides by the soils from both CnT and CT plots is currently under investigation.

2.6 Conclusions

Examinations of characteristics of LF material of a Norfolk soil under long term CnT and CT management indicated that tillage can influence the distribution of LF in soil profile. CnT treatment favored the build-up of surface plant residue which consequently increased the SOC and soil TCN contents in the top soil (0-5 cm). The CT treatment, on the other hand, mixed residue within the 15 cm soil layer. As a result, SOC and LF contents were higher at the deeper layers (5-15 cm) than CnT. The elemental composition of HA from two tillage systems was similar, but one cannot rely on elemental composition only in evaluating management effect. The solid-state ^{13}C NMR results clearly demonstrated that the aliphatic C content of HA was higher in the top soil (0-5 cm) under CnT than CT. Conversely, the aromatic C of HA was higher in the top soil (0-5 cm) under CT than CnT. Aliphatic C of HA declined with the increase of soil depth under both tillages, whereas the aromatic C of HA increased with soil depth. Although DRIFT spectra of HA were similar in their basic peak assignment, HA O/R ratio from the top soil (0-5 cm) of CnT treatment was higher than that from CT treatment, indicating that HA contained more recalcitrant functional groups in CT tillage. In sum, tillage management can substantially change the quantity and quality of SOM as reflected by relatively high contents of LF materials and more biologically active SOM in soils under CnT. Structural changes of SOM may change the sorptive behavior of pesticides in soils and their fates, efficiency, and uses. Future research has to

address the relationship between spectroscopic characteristics and their agricultural significance.

Table 2.1. Organic carbon, total combustible nitrogen and light fraction in the soil under different tillage systems (standard deviation in parentheses)†

	Soil depth	CnT	CT
	Cm	kg m^{-2}	
SOC	0-5	2.30 (0.02)a‡	1.22 (0.01)a
	5-10	0.89 (0.01)b	1.23 (0.01)a
	10-15	0.61 (0.01)b	0.81 (0.01)b
TCN	0-5	0.22 (0.01)a	0.11 (0.00)a
	5-10	0.08 (0.01)b	0.11 (0.00)a
	10-15	0.05 (0.00)b	0.06 (0.00)b
LF	0-5	1.19 (0.02)a	0.63 (0.01)a
	5-10	0.17 (0.01)b	0.55 (0.01)a
	10-15	0.10 (0.00)b	0.12 (0.00)b
		C/N ratio of Soil	
C/N	0-5	10.4 (0.02)a	11.1 (0.01)a
	5-10	11.1 (0.02)a	11.2 (0.01)a
	10-15	12.2 (0.02)a	13.5 (0.03)a
		g kg^{-1}	
LF-OC/SOC	0-5	160 (4.01)a	150 (3.48)a
	5-10	40 (1.55)b	130 (2.78)a
	10-15	42 (1.78)b	42 (1.29)b
LF-N/TCN	0-5	100 (2.45)a	90 (2.07)a
	5-10	30 (1.38)b	80 (2.17)a
	10-15	22 (1.29)b	22 (1.69)b

†Aerial mass of SOC, TCN, and LF was calculated from area and soil bulk density.
‡Means with different letters are significantly different P = 0.05

Table 2.2. Elemental composition of humic acids on an ash-free basis and atomic H/C and C/N ratios

Sample	Depth (cm)	C	H	N	H/C	C/N
		g kg^{-1}				
CnT	0-5	527	41	39	0.94	15.7
CnT	5-10	479	36	31	0.92	18.1
CnT	10-15	516	35	31	0.81	19.4
CT	0-5	546	40	37	0.88	17.2
CT	5-10	548	40	35	0.88	18.3
CT	10-15	538	40	31	0.89	20.3

Table 2.3. Ratios of selected peak heights from DRIFT spectra of humic acids (Wander and Traina, 1996b)

HA	Depth (cm)	R_1 (O/R) $\frac{1727+1650+1160+1127+1050}{2950+2924+2850+1530+1509+1457+1420+779}$	R_2 $\frac{1727}{1457+1420+779}$
CnT	0-5	0.87 (0.02)a†	0.51 (0.02)a
CnT	5-10	0.69 (0.01)b	0.44 (0.02)b
CnT	10-15	0.70 (0.01)b	0.43 (0.02)b
CT	0-5	0.74 (0.01)ab	0.44 (0.02)a
CT	5-10	0.69 (0.01)b	0.42 (0.01)a
CT	10-15	0.67 (0.01)b	0.43 (0.01)a

†Means with different letters are significantly different P = 0.05

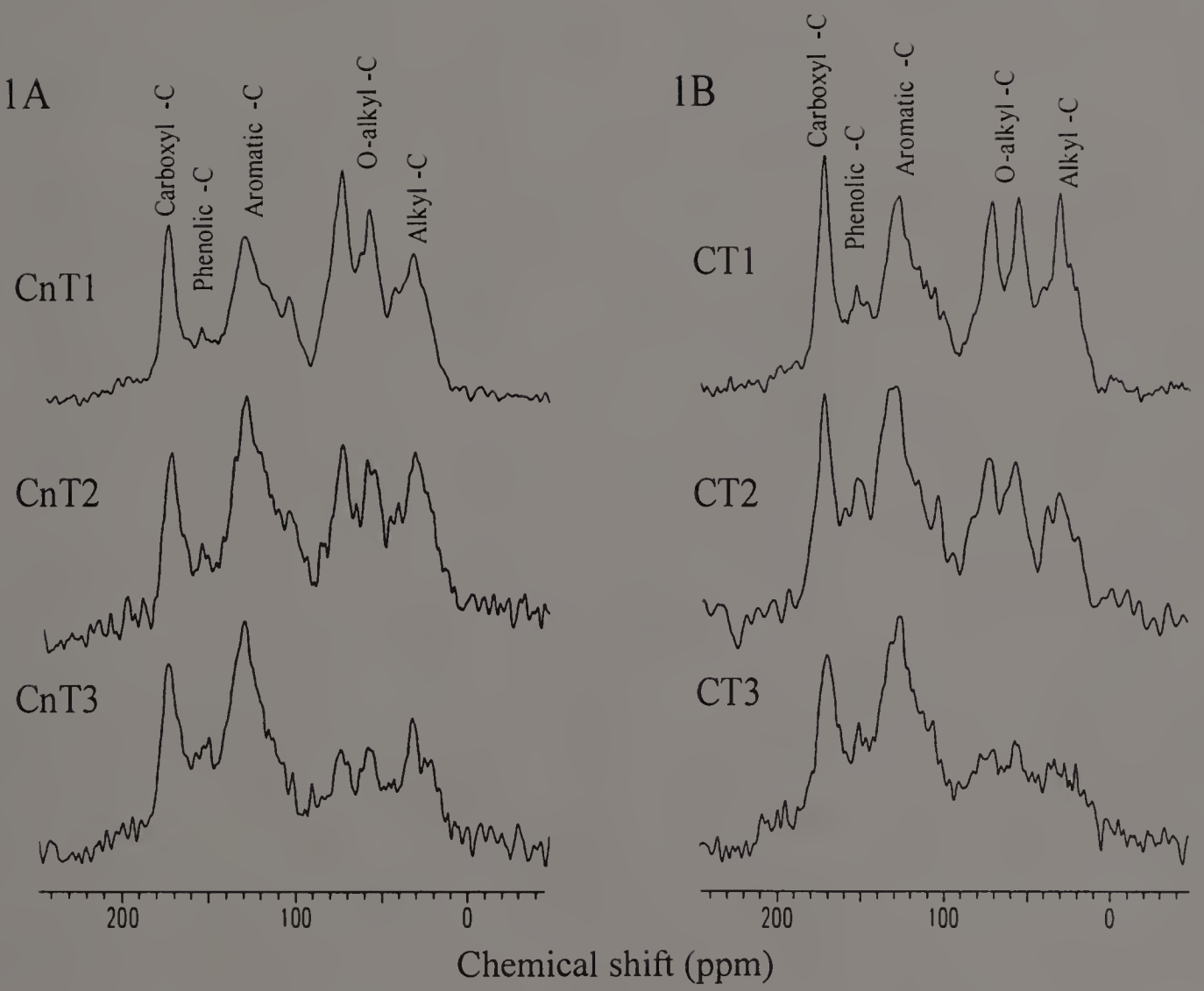
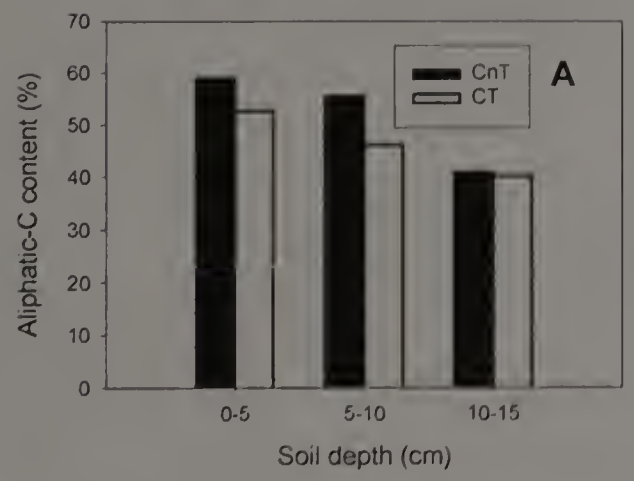
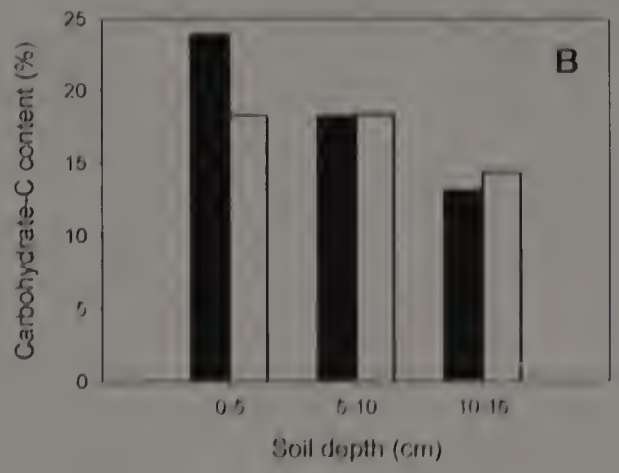
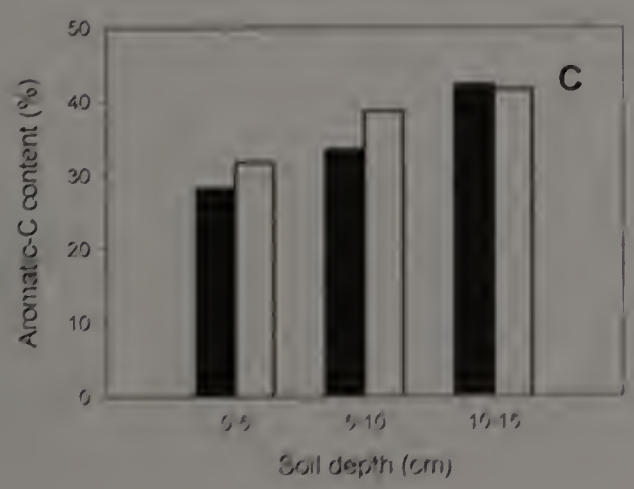


Figure 2.1 CPMAS-TOSS C-13 NMR spectra of HA in a Norfolk soil under different tillages







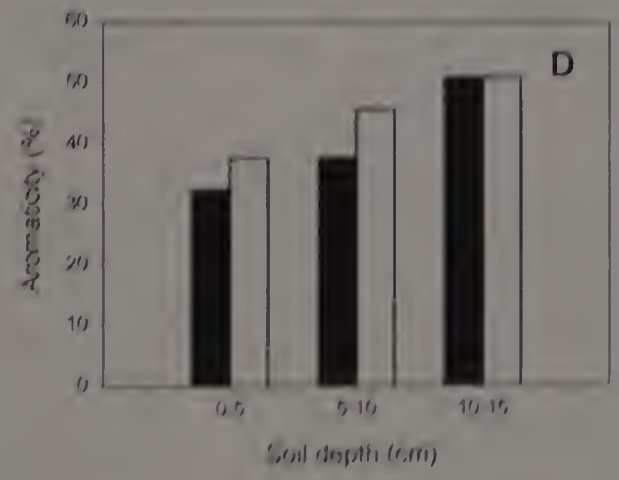
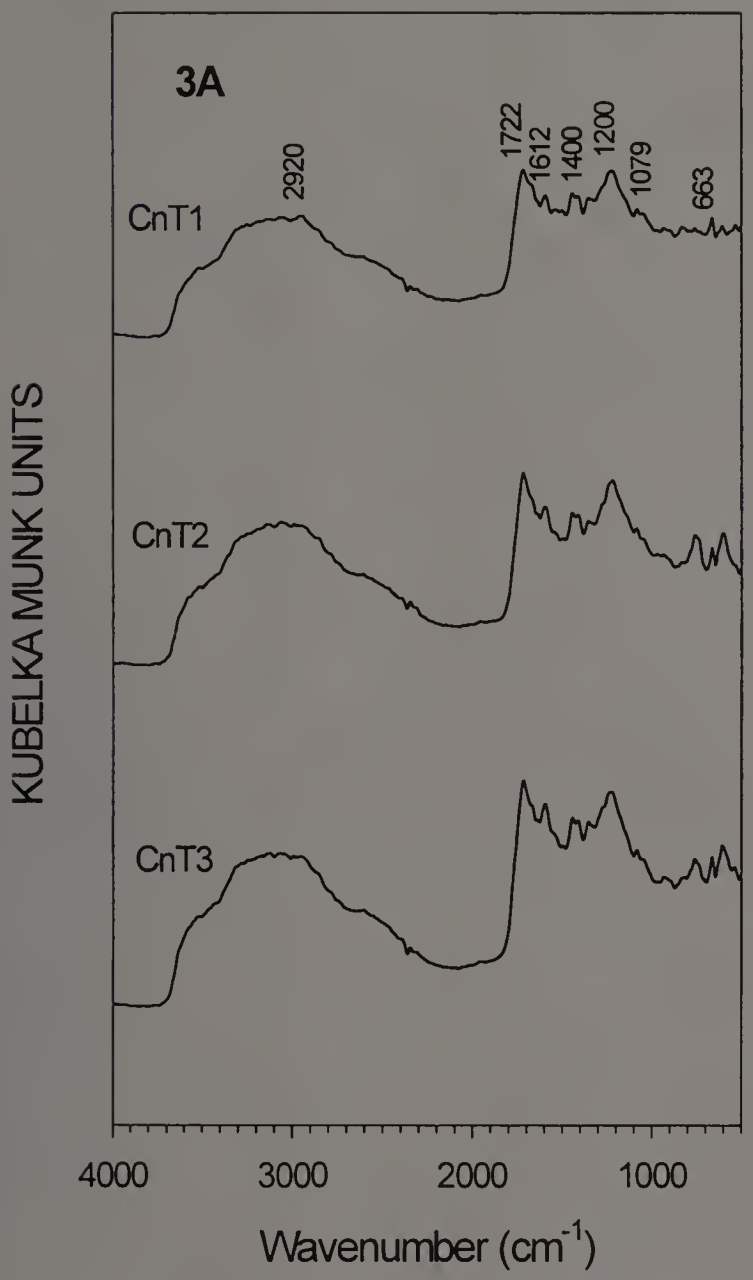


Figure 2.2. Solid-state ^{13}C NMR HA data under different tillage systems



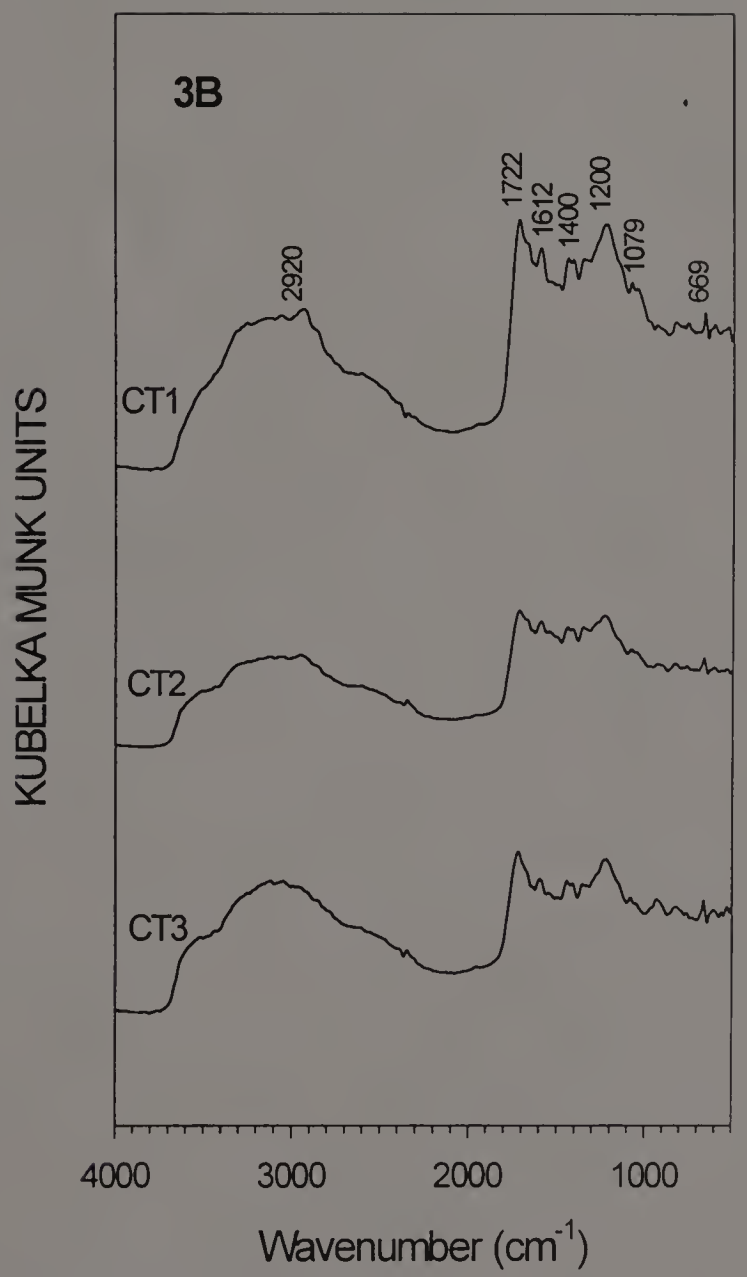


Figure 2.3 DRIFT spectra of HA under different tillage systems

CHAPTER 3

INFLUENCE OF COVER CROP MANAGEMENT SYSTEMS ON SOIL ORGANIC MATTER

3.1 Abstract

Characterization of soil organic matter (SOM) is important for determining the overall quality of soils and cover crop system may change the SOM characteristics. The purpose of this study was to examine the effect of cover crops on the chemical and structural composition of SOM. We isolated humic substances (HS) from soils with following treatments: a) Vetch (*Vicia Villosa* Roth.)/Rye (*Sesale cereale* L.), b) Rye alone, and c) Check (no cover crops) that were treated with various nitrogen fertilizer rates. CP-TOSS (Cross-Polarization and TOtal Sideband Suppression) ^{13}C NMR results indicate that humic acids (HA) from rye cover alone were more aromatic and less aliphatic in character than the other 2 cover crop systems without nitrogen fertilizer treatment. Based on the DRIFT spectra peak O/R ratios, the intensities of oxygen-containing functional groups to aliphatic and aromatic (referred to as recalcitrant) groups, the highest ratio was found in the HA from the vetch/rye system with nitrogen fertilizer. The lowest ratio occurred at the vetch/rye system without nitrogen fertilizer treatment. The O/R ratio of fulvic acids (FA) can be ranked as: vetch/rye without fertilizer > vetch/rye with fertilizer > no cover crop without fertilizer > rye alone (with or without fertilizer). Both organic carbon (OC) and light fraction (LF) contents were higher in cover crop treatments with and without nitrogen fertilizer than that of no cover crop system. These chemical and spectroscopic data show that cover crop systems had a profound influence on the soil HS and LF characteristics.

3.2 Introduction

Soil organic matter (SOM) is a very reactive, ubiquitous component in soils. It is an important soil quality attribute, which influences the productivity and physical well-being of soils. Cover crops can play an important role in nutrient management. Cover-crop systems are becoming increasingly important as attention is focused on nonpoint sources of nutrient pollution. Thus, it is important from both an economic and environmental standpoint, to determine how cover crop systems will influence soil quality and the biogeochemical cycling of carbon.

SOM contents and properties are a function of agricultural practices and the amounts and kinds of plant residues returned to the soil (Mann, 1985; Doran et al., 1987; Cheshire et al., 1990; Campbell et al., 1999). Based on data from long-term research plots in the U.S.A., Doran (1980) reported that numbers of microbes, microbial biomass and potentially-mineralizable nitrogen were greater for no-tillage than for conventional tillage in the 0-7.5 cm depth. However, these trends were generally reversed in the 7.5-15 cm depth, probably because conventional tillage moves some SOM to lower soil depths which benefits microbial growth. Consequently, when the top 15 to 30 cm of soil under no-tillage is considered, often no net effect was observed (Doran, 1980; Angers et al., 1997). Wander and Traina (1996a) showed that SOM in crop rotation with cover crops was significantly higher than those rotations without cover crops. However, Lal et al. (1991) in a similar type of study reported no or minimal change of SOM content. The reason for not detecting any SOM change could be due to natural soil heterogeneity (Wander and Traina, 1996a). It is well known that continuous

cultivation under a cereal crop rotation results in substantial losses of soil C and N (Dormmar 1979; Campbell and Souster, 1982; Dalal and Henry 1988; Campbell et al., 1991; Paustian et al., 1992). However, studies of organic matter using ^{13}C nuclear magnetic resonance (NMR) spectroscopy have generally indicated that the chemical nature of the remaining C shows little change as a result of cultivation and that the stability of SOM appears to depend more on physical protection mechanisms than in any inherent recalcitrance of the organic structures (Skjemstad et al., 1986; Skjemstad and Dalal 1987; Oades et al., 1988; Capriel et al., 1992).

In addition to SOM quantity, the quality (*e.g.*, structure and composition) and distribution of individual fractions (*e.g.*, humic acids, polysaccharides) are essential to the maintenance of soil productivity. Monreal et al. (1995) observed a higher lignin dimer to lignin monomer ratio in continuous wheat rotation and this ratio decreased from large to small aggregate sizes, indicative of the change in the quality of SOM. Wander and Traina (1996b) used diffuse-reflectance Fourier transform infrared (DRIFT) spectroscopy to examine functional groups of SOM fractions and reported that the ratios of reactive to recalcitrant fractions in HA best reflected overall SOM bioavailability. They also reported that the ratios in FA, LF and litter were useful in distinguishing temporal impacts of farming systems on SOM lability. They concluded that the characteristics and distribution of individual SOM fractions may provide a means for assessing management impacts on SOM quality that can be tied to soil productivity, and they specifically emphasized that further work is needed to determine how SOM composition changes with tillage and cropping practices.

DRIFT detects molecular vibrations and is useful for functional group analysis and for identification of molecular structures of SOM (Stevenson, 1994). But it cannot be used to quantify carbon contents of structural groups (*e.g.*, aromatic structure). In contrast, ^{13}C NMR spectroscopy provides quantitative data for structural components (Mao et al., 2000). NMR has been successfully used to characterize SOM by many scientists (Wilson, 1987; Schnitzer et al., 1991; Xing et al., 1994; Preston, 1996; Xing and Chen, 1999; Ding et al., 2002). Thus, it would be advantageous to use both NMR and DRIFT to characterize SOM and compare quantitative data of SOM under different cover crop systems.

The primary objective of this research is to gain a better understanding of the impact of cover-crop systems on SOM. We chose to examine SOM fractions obtained using alkali-extraction (HA and FA) and physical fractionation (LF). The specific objectives are: 1). to determine structural and compositional changes of HS (HA and FA fractions) caused by cover-crop systems using NMR and DRIFT, and 2). to evaluate the light fraction variability as affected by cover-crop systems with or without nitrogen fertilizer treatment.

3.3 Materials and Methods

Site description and sampling

Since 1990, cover crop experiments have been conducted in the Connecticut River Valley at the Massachusetts Agricultural Experiment Station Farm in South Deerfield, Massachusetts (U.S.A). The soil in these plots is a fine sandy loam (coarse, mixed, mesic Fluventic Dystrudept) and low in SOM (~2%). Its upper 0.6 m is homogeneous, overlaying inclined layers of coarse and fine material to great

depth. It is a typical soil in the intensively cropped Connecticut River Valley in Massachusetts. Three cover crop treatments with four nitrogen rates (applied to the corn crop after cover crop incorporation) were laid out in a complete factorial design in bordered 3 m x 7.5 m in small plots in four randomized blocks. Cover crop treatments and seeding rates were:

(i) check (no cover crop)

(ii) rye (125 kg/ha)

(iii) hairy vetch + rye (46 + 65 kg/ha)

Nitrogen fertilizer rates were 0, 67, 135, 202 kg N/ha using NH_4NO_3. Cover crops were seeded yearly on the same plots in early September and were cut using a flail mower at the end of May. Then the plots were rotor-tilled to a depth of 15 cm to incorporate cover crops into the soil for corn seedbed preparation. Corn was seeded in the first week of June and harvested in the last week of August. After harvest, corn stalks were also cut using a flail mower and disk-harrowed to a depth of 15 cm. Biomass of cover crops and corn was determined and recorded each year. Samples were collected from the top (0-25 cm) soil using a 10 by 5 cm core sampler. In each plot, 15 cores were drawn and combined to form a plot composite. Soils were stored at 4 ^{o}C while in transit and maintained field moist until processed. Detailed soil sample information is listed in Table 3.1.

Density gradient separation of light fraction (LF) material and humic substances (HS) extraction

The LF material from each soil sample was isolated using a modified density gradient method of Wander and Traina (1996a). Three sequential densitometric

rinses were obtained by dispersing (1:1 w/v) of 50 g soil in a NaBr solution (density 1.6 g/ml). The soil was shaken for 30 min and centrifuged at 8000 rpm for 20 min. These rinses were then transferred into a 250 ml separatory funnel and allowed to settle overnight. The heavy SOM fraction which settled to the bottom of the funnel was removed and the LF material was filtered using a 0.45 μm polycarbonate membrane filter. The weight yield of light fraction was measured and the light fraction-organic carbon (LF-OC) and total combustible nitrogen content were determined using the LECO-CN 2000 analyzer.

Soil samples were air-dried and passed through a 2 mm sieve before HS extraction. The extraction procedures followed the methods by Chen and Pawluk (1995) for humic acids (HA) and Ding et al. (2001a) for fulvic acids (FA).

Diffuse reflectance Fourier transform infrared (DRIFT) analysis

DRIFT was performed in an Infrared Spectrophotometer (Midac series M 2010) with a DRIFT accessory (Spectros Instruments). All SOM fractions were powdered with a sapphire mortar and pestle and stored over P_2O_5 in a drying box. Humic and fulvic acid concentrations for this determination ranged from 2 to 4 mg and were supplemented with KBr to a total weight per sample of 100 mg, and then, ground with an agate mortar and pestle. The milled sample was immediately transferred to a sample holder, its surface was smoothed with a microscope glass slide. Before analysis, the diffuse-reflectance cell containing the samples was flushed with nitrogen gas to eliminate interference from carbon dioxide and moisture. A small jar (20 ml) containing anhydrous $Mg(ClO_4)_2$ was placed inside the sample compartment to further reduce atmospheric moisture.

To obtain DRIFT data, 100 scans were collected at a resolution of 16 cm^{-1} and spectra, as well as numerical values for major peaks' wave-numbers and intensities, were recorded. The background consisted of powdered KBr was scanned under the same environmental conditions as the sample-KBr mixtures. Absorption spectra were converted to a Kubelka-Munk function using Grams/32 software package (Galactic Corporation). Peak assignments and intensity (by height) ratio calculation were done following the methods of Baes and Bloom (1989), Niemeyer et al. (1992), Wander and Traina (1996b), and Ding et al. (2002).

Solid-state ^{13}C NMR spectroscopy

CP-TOSS (Cross-Polarization and Total Sideband Suppression) was used to obtain all ^{13}C NMR spectra. Samples were run at 75 MHz (^{13}C) in a Bruker MSL-300 spectrometer. HA was packed in a 7-mm-diameter zirconia rotor with a Kel-F cap. The spinning speed was 4.5 kHz. A ^{1}H 90° pulse was followed by a contact time (t_{cp}) of 500 μs, and then a TOSS sequence was used to remove sidebands (Schmidt-Rohr and Spiess, 1994; Xing et al., 1999). The 90° pulse length was 3.4 μs and the 180° pulse was 6.4 μs. The recycle delay was 1 s with the number of scans about 4096. The details are reported elsewhere (Xing et al., 1999).

Statistical analyses

All data presented are the mean of at least three replicate measurements, except of solid state ^{13}C NMR data because of the high cost per sample and low availability of the instrument. However, preliminary NMR measurements with one HA showed minimal variations, which is consistent with the results of an extensive NMR study conducted in our laboratory (Mao et al., 2000). A two-way Analyses of

Variance (ANOVA) was used to analyze cover crop system and nitrogen fertilization effects on SOM. Cover crop system and nitrogen rate were the experimental factors. SigmaStat software (SPSS Corp., Richmond, CA) was used for each test at a 0.05 level of significance.

3.4 Results

Yields of organic carbon and light fraction materials

The quantity of organic carbon (OC) determined from soil under different cover crop systems is calculated on a soil volume basis (Table 3.2). With no nitrogen fertilizer, the OC content is the highest in the vetch/rye system and lowest in the soil without cover crop. After 9 years field experiment, OC differences are significant between the cover crop systems (both vetch/rye and rye alone) and no cover crop systems. The OC is significantly affected by the nitrogen fertilizer application. The OC in both vetch/rye and no cover crops with nitrogen fertilizer is 13 kg m^{-3}. The OC in rye alone with fertilizer is 16 kg m^{-3}, which is significantly higher than the vetch/rye and no cover crop systems. Total combustible nitrogen (TCN) shows the similar trend for all three different cover crop systems with or without nitrogen fertilizer treatment. The C/N ratios of the soil are not significantly affected by cover crop and nitrogen fertilizer treatments.

Cover crop treatments also significantly influence LF content (Table 3.2). Again, without nitrogen fertilizer, LF is the greatest in soil from vetch/rye, intermediate in rye alone soil, and the least in the soils with no cover crops. With nitrogen fertilizer treatment, the highest LF content is in the vetch/rye plots, followed by rye alone cover, and the soil without cover crop has a significantly

lower LF pool than the other two. The amount of OC in LF varies between 21 and 27%. In both with or without nitrogen fertilizer treatments, the LF-OC% is the greatest in rye alone soil, intermediate in vetch/rye plot, and the lowest in the soil without cover crops. There is a significant difference of LF-OC% between cover crop and no cover crop systems. Compared to the whole soil, the C/N ratios of the LF are distinctly higher. Without nitrogen fertilizer treatment, the highest C/N ratio of LF appears in rye alone system, significantly higher than other two treatments. However, with nitrogen fertilizer treatment, the vetch/rye plot has the greatest C/N ratio, but not significantly different from other two systems.

Solid-state ^{13}C NMR spectra

Although CP-TOSS spectra cannot be used for absolute quantitation, they could be compared in this study because all of the HA samples were run under the same conditions and from the same type of soil. Functional group assignments are reported elsewhere (Stevenson, 1994; Preston, 1996). The six soil HA NMR spectra are quite similar in peak position and intensity (Fig. 3.1). They exhibit several distinct peaks in the aliphatic (0-108 ppm), aromatic (108-162 ppm) and carboxyl (162-190 ppm) regions. The peak at 31-33 ppm is long alkyl chains $(CH_2)_n$. The aromatic region contains a large peak at about 131 ppm. This resonance signal is assigned to ring carbons in which the ring is not substituted by strong electron donors such as oxygen and nitrogen (Schnitzer and Preston, 1986). Alkyl benzenes are typical components which can yield such resonance. Therefore, it appears that in the HA, a large proportion of the aromatic carbon is not substituted by oxygen and nitrogen. The small peak at approximately 155 ppm is

the presence of oxygen- and nitrogen-substituted aromatic C groups (phenolic OH or aromatic NH_2). The large peak near 175 ppm is due to carboxyl groups associated with carboxylic acids, amides, and esters.

Visual comparison of the six HA spectra displays little difference that can be described in terms of presence or absence of specific peaks (Fig. 3.1). There are, however, some differences in relative signal intensity. Carbon distribution in aliphatic groups (0-108 ppm) is showed in Figure 3.2A. An examination of the data shows that HA from rye alone system differs from the other HA in aliphatic region and the carbon content of the rye alone plot in this region is the lowest without nitrogen fertilizer. The aliphatic-C of the vetch/rye without nitrogen fertilizers is 55.3%; and 48.9% for rye alone without nitrogen fertilizers (Fig. 3.2A). The alkyl region (0-50 ppm) shows the similar trend as for the aliphatic region (Fig. 3.2B). With or without nitrogen fertilizer treatment, the alkyl carbon changes are minimal for both vetch/rye and rye alone systems even though the alkyl carbon content is higher in vetch/rye soil than in rye alone treatment. The alkyl carbon content is higher in control (no cover crop system) without nitrogen fertilizer than with nitrogen fertilizer.

The phenolic-C (145-162 ppm) of HA for rye alone systems with or without nitrogen fertilizers is slightly higher than that of vetch/rye cover systems (data not shown). We found that phenolic-C is higher in the no cover crop system with nitrogen fertilizer than without nitrogen fertilizer. The HA extracted from rye alone system, compared with vetch/rye cover systems with or without nitrogen fertilizers, is relatively enriched in aromatic-C (108-145 ppm) (Fig. 3.2C). The aromatic-C of

HA from both vetch/rye and rye alone treatments is higher without nitrogen fertilizer treatment than with nitrogen fertilizer. Conversely, the HA aromatic-C for no cover crop treatments, is greater with nitrogen fertilizer than without nitrogen fertilizer treatment.

The aromaticity (expressed in terms of aromatic-C as a percentage of the aliphatic + aromatic) of HA is higher in rye alone system with or without nitrogen fertilizer than vetch/rye treatments (Fig. 3.2D). Furthermore, the HA aromaticity of both vetch/rye and rye alone systems is greater in the plots without nitrogen fertilizer treatment than that with nitrogen fertilizer. The reverse trend is true for no cover crop systems.

DRIFT spectroscopy of HA and FA

Wavenumbers and assignments for peaks in DRIFT are the same as in IR and FTIR spectroscopy (Fuller and Griffiths, 1978; Baes and Bloom, 1989; Niemeyer et al., 1992; Stevenson, 1994; Ding et al., 2000). All peaks in our HA and FA are similar to the typical HA and FA spectra, respectively as reported in the literature. The spectra of the six HA and FA are presented in Figures 3.3 and 3.4 respectively. In general, the resolution of the spectra shows a significant improvement, compared with previously published spectra using dispersive or FTIR spectrophotometers (Baes and Bloom, 1989). The peaks at 1715 to 1730 cm^{-1} (mostly COOH groups), at 1620 cm^{-1} (mostly aromatic-C), and at 1200 cm^{-1} (mostly OH or COOH) are distinct and sharp in all our spectra.

The HA exhibits the most distinct COOH bands in both 1720 and 1200 cm^{-1} regions (Fig. 3.3). The high intensity of these bands is a typical characteristic of

HA. and their presence reflects the high solubility and acidity. Slight deviations from the expected lines. which appear as "valleys" (sometimes referred to as negative bands. Niemeyer et al.. 1992). are seen in some of the spectra at the wavenumbers between 3000 to 3700 cm^{-1}. These bands are of low intensity and appear in regions of little importance to humic material. The position and number of peaks below 1550 cm^{-1} are affected by the substitution patterns of the HA's precursor molecules (Baes and Bloom, 1989: Niemeyer et al.. 1992). This is probably due to the incorporation of precursor molecules in an unaltered configuration. Such an effect is illustrated by the presence of peaks or shoulders at 1550. 1470. and 780 cm^{-1}. corresponding to ring vibrating modes of ortho-substituted aromatics (Bellamy. 1975).

Assignment of the OH stretching band to phenolic OH rather than an aliphatic alcoholic OH is supported by the C-OH stretching band centered about 1250 cm^{-1} which is characteristic of oxygen on an aromatic ring. The center of the band is much more apparent in the HA compared to the FA spectra. The C-OH stretching vibration of phenolic OH occurs at frequencies above 1200 cm^{-1}. Aliphatic alcohols. however. are characterized by broad and intense C-OH stretching bands at lower frequencies (1015-1150 cm^{-1}) (Conley, 1972).

All DRIFT spectra of each fraction are similar in their basic peaks. For example, the DRIFT spectra of FA fractions from all treatments have the same functional groups (Fig. 3.4). It is a common practice to draw conclusions on factors affecting SOM composition by using a single spectrum of composite fractions. However. this method does not provide the kind of detailed information required to

ascertain cover crop management effect on SOM. Therefore, detailed insight on the reactivity of HA and FA is provided by calculation of O/R ratios, which are the intensities of oxygen-containing functional groups vs. aliphatic and aromatic (referred to as recalcitrant) groups (Niemeyer et al., 1992; Wander and Traina, 1996b). The reactivity of SOM is related with organic oxygen because it is present in all major functional groups, e.g., carboxyl, phenolic, hydroxyl, alcohol, and carbonyl and can be associated with SOM binding characteristics. The impact of cover crop system on spectral composition is summarized in the peak ratio (i.e., O/R ratios) tables (Tables 3.3 and 3.4).

The HA fraction isolated from the vetch/rye plot with nitrogen fertilizer has the highest ratio R_1 (Table 3.3), significantly different from rye alone and no cover crop systems. There is no statistically significant difference of R_1 between rye alone and no cover crop with nitrogen fertilizer. The R_1 ratio is the highest with no cover crop without nitrogen fertilizer, followed by rye alone and vetch/rye cover treatments. The higher R_1 ratio in vetch/rye with nitrogen fertilizer may suggest that vetch/rye system contains more oxygen-containing functional groups with fertilizer treatment than that of without fertilizer treatment. The relatively high O/R ratios of the HA support the notion that SOM in the vetch/rye cover with nitrogen fertilizers is more biologically active.

In contrast to the O/R ratios of HA, the FA total O/R peak ratio ((1850+1650+1400+1080+560)/(3340+2924+1535+1457)) is greater in the vetch/rye without fertilizer treatment than with fertilizer (Table 4.4). Meanwhile, the ratios from both the vetch/rye treatments are significantly higher than rye alone

treatments. The O/R ratios of FA do not differ much between the rye alone and no cover crop system with nitrogen fertilizer. When comparing the R_1 ratios of HA with total O/R ratios of FA in different cover crop systems, HA R_1 from both the vetch/rye and rye alone systems is higher with nitrogen fertilizer treatment than without nitrogen fertilizer, while the reverse is true for the total O/R ratios of FA. Both HA R_1 and FA total O/R ratios of no cover crop system are higher in soils without nitrogen fertilizer than with nitrogen fertilizer. Those results suggests that cover crop systems (with or without nitrogen fertilizer) affect the HA and FA compositions.

3.5 Discussion

Cover crops have long been recognized to play an important role in sustainable agriculture due to their functions in preventing soil erosion, improving soil productivity, contributing nutrients to succeeding crops, and suppressing weeds. However, the relationship between SOM characteristics and cover crop management practices is poorly understood. Although the mechanisms affecting the sequestration of organic matter in soil are complex (Campbell and Souster, 1982; Doran et al., 1987; Campbell et al., 1999), it is clear that the different types of plant residues do not contribute to the same extent to humus formation and that intrinsic biodegradability is a key factor related to the microbial activity (Campbell et al., 1991).

Quantitative changes in SOM are associated with accumulation of C and N in the vetch/rye and rye alone cover systems (Table 3.2). This condition is obviously due to the lack of incorporation of plant residue into the soil under the no cover

crop system, and is consistent with other reports (Campbell and Souster, 1982; Campbell et al., 1999). With nitrogen fertilizer treatment, the highest OC and TCN contents appear under the rye alone system rather than vetch/rye system. This means that nitrogen fertilizer had a significant influence on rye biomass input but had little, if any, effect on vetch biomass production. A field study by Torbert et al. (1996) on a Norfolk loamy sand soil in east-central Alabama showed that nitrogen fertilization increased biomass production for rye, whereas very little increase was observed for the clovers owing to nitrogen fixation. They also reported that the biomass production of rye had a linear relation with the amount of nitrogen fertilizer applied.

The LF material consists largely of plant residues in varying stages of decomposition and varies in physical size. The LF has been used as an indicator of changes in labile organic matter as affected by tillage, crop rotation, and environmental factors (Campbell et al., 1999). In other words, characterizing the size of the active pool, as well as its C and N contents, may show changes due to management practice more rapidly than measuring changes in the magnitude of the whole SOM pool (Monreal et al., 1995; Wander et al., 1994). Large variation in LF contents (Table 3.2) implies that the cover crop system with different nitrogen fertilizer rates has significantly influenced (at or < 0.05 level) the percentage of SOC isolated as LF material. Significant differences in the LF distribution with nitrogen fertilizer treatments support the notion that the two cover crops may hold different organic matter pool sizes. Vetch has a larger readily decomposable pool, while the rye may have a larger recalcitrant pool, which is confirmed by our ^{13}C

NMR data that HA from rye alone cover has more aromatic-C than vetch/rye systems (Fig. 3.2C). Furthermore, HA total O/R ratio (R_1) from DRIFT spectra indicates that there is a significant difference between vetch/rye and rye alone treatments (Table 3.3), demonstrating that SOM from vetch/rye treatments is more biologically active than from rye alone cover with nitrogen fertilizer. Thus, DRIFT and ^{13}C NMR can be used as complementary methods for the characterization of HS.

The decomposition and mineralization kinetics are determined by residue and soil characteristics, residue characteristics include N content, C chemistry, particle size, and quantity added (Lal et al.; 1991). Important soil characteristics include soil texture, pH, aeration, and for low nutrient residues, soil nutrient status. After determining dry matter losses of cover crop residues during decomposition in the field, Liu (1997) reported that hairy vetch had a significantly faster rate of decomposition than rye. High decomposition rates in the vetch system is a indicator of the rapid decay of carbohydrates, protein, and other low C:N ratio compounds. Low decay rates in rye systems are representative of slow decomposition of recalcitrant materials such as lignin. Plant residues with high nitrogen content showed high decomposition rates and nutrient release (Liu, 1997). The negative effect of polyphenols on decomposition of organic matter and nutrient release was reported by Vallis and Jones (1973). Negative correlations were also observed between decomposition rate constants and C:N ratio, percent lignin and polyphenol content of plant residues (Tian et al., 1995). With further humification, HA from rye systems may become more aromatic.

Agricultural tillage and crop management practices of soils contribute to a reduction in C/N ratio (Stevenson, 1994). For instance, mean C/N ratio is 13:1 in agricultural soils whereas that of virgin soils is approximately 20:1. According to Kaffka and Kopth (1989), reduced C/N ratios of mineral soils are associated with the loss of labile carbon and consequently reduced productivity. The relatively high C/N ratio in LF (Table 3.2) of the rye alone system without nitrogen fertilizer may suggest that this soil has the lowest inherent nitrogen supply potential. This result may suggest that soil nitrogen availability is the main limitation for non-legumes. With nitrogen fertilizer treatment, nitrogen content in LF of the rye system is the highest, indicating that nitrogen fertilization contributes to a larger increase in total N uptake for rye than for other two systems. However, without nitrogen fertilizer the nitrogen content of vetch/rye plot in LF is significantly higher than rye alone plot. It is consistent with the results obtained by Torbert et al. (1996). Legumes utilize both soil nitrogen and atmospheric nitrogen gas in meeting their nitrogen requirements. If the soil does not have enough nitrogen they can fix atmospheric nitrogen to meet their requirements. They further reported that total nitrogen content of rye had a direct linear relation with nitrogen application, while the total nitrogen content of clover plants was not affected by nitrogen fertilizer application, but the proportion of nitrogen in the plant from nitrogen gas fixation was reduced by application of nitrogen fertilizer.

On the basis of these observations, and from data published in the literature (Skjemstad et al., 1992), we can conclude that the HA from rye cover alone may contain less oxygen-alkyl (polysaccharides) groups than HA from vetch/rye cover

system. Thus, the HA may be more humified in rye cover system than that in vetch/rye system. Our results suggest that HA from rye alone system may contain more tannins and lignins than vetch/rye treatment because tannins and lignins are the main contributors in the aromatic and phenolic regions (Preston, 1996). Another distinguishing feature of the intensity distribution is that fertilization is associated with a small decrease of aliphatic-C and increase of aromatic-C content within no cover crop treatments (Figs. 3.2A and 3.2C). One possible explanation is that the use of nitrogen fertilizer has a strong effect on the decomposition and polymerization processes of SOM. Perhaps it lowers the C:N ratio of debris, promoting decomposition of plant residues and formation of HS.

FA has relatively low molecular weights and higher oxygen contents, and as a result is more polar and mobile than HA. Thus, FA may be representative of the more available organic matter pool (Stevenson, 1994; Wander and Traina, 1996b). The total O/R ratios from both vetch/rye treatments are significantly higher than rye alone treatments. This implies that FA fractions from vetch/rye system are more chemically or biologically active than from rye alone system. As the O/R ratios of FA are not much differed between the rye alone and no cover crop system with nitrogen fertilizer, the FA fractions may undergo a similar change for these two management systems either by chemical oxidation or as a microbial source.

Soil minerals and SOM are the major components for sorption of organic chemicals including pesticides (Xing, 1997 ; Xing and Chen, 1999). Agricultural practices generally do not substantially change contents and characteristics of soil mineral component due to their inert chemical nature, for example, there are no

marked differences in clay contents between conservation tillage and conventional tillage plots after 18 years (Novak et al., 1996). However, soil management can change quantity and characteristics of SOM as presented above. Sorption increases with elevated levels of SOM and reduce leaching potential. Nanny and Maza (2001) reported that the percent aromaticity of the HA and FA and the solution pH influence the extent of noncovalent interactions with monoaromatic compounds. For example, benzene interacts with dissolved HA at all pH values; however, these interactions increase with decreasing pH and generally are proportional with the HA percent aromaticity.

Sorption of hydrophobic compounds to SOM has been shown to directly related to the percent aromaticity and inversely related to the SOM polarity. Organic matter with high aromaticity sorbs more aromatic compounds such as benzene and xylene (Xing, 1994b). Furthermore, sorption of benzene, xylene, and naphthalene is inversely related to polarity of SOM expressed as a mass ratio of (N + O)/C (Xing, 1994b). Therefore, the changes of the quantity and quality of SOM by cover crop systems may potentially alter sorption behavior, mobility, and biological activity of pesticides in soils.

3.6 Conclusions

Organic carbon is higher in soils under both a vetch/rye and rye alone management systems than under no cover crop system. This is due to low input of plant residues into the soil under no cover crop system. Yields of LF material under different cover crop systems are strongly dependent on the nitrogen fertilizer rates. For no nitrogen fertilizer treatments, LF content changes are minimal. However,

with nitrogen fertilizer treatments, the LF content changes are substantial under different cover crop systems. Although DRIFT cannot be used to quantify the absolute C contents of structural groups, it can be used to generate peak ratios from which we can assess the relative enrichment or depletion of specific functional groups. All DRIFT spectra of each fraction are similar, but cover crop systems and nitrogen fertilizer rates changed the O/R ratios of HA and FA. The CP-TOSS ^{13}C NMR data show that there are no major differences among the 6 HA spectra in terms of the number and position of peaks. However, by calculating aliphatic- and aromatic-C contents, the HA extracted from rye alone is more aromatic and less aliphatic than HA extracted from vetch/rye, indicative of the impact of the cover crop systems on the structure and composition of humic substances. Further research is needed to illustrate how these SOM changes (composition and structure) are related to soil property, productivity, and pesticide sorption.

Table 3.1. Soil samples from South Deerfield Massachusetts[†]

Sample Number	Depth (cm)	Cover crops	Nitrogen rates (kg N ha^{-1})
VR1	0-25	Vetch/Rye	0
VR4	0-25	Vetch/Rye	202
RA1	0-25	Rye Alone	0
RA4	0-25	Rye Alone	202
C1	0-25	No Cover Crops	0
C4	0-25	No Cover Crops	202

[†] Samples were collected only from the plots with 0 and 202 kg N ha^{-1} treatments.

Table 3.2. Organic carbon and total combustible nitrogen in the soil and light fraction under different cover crop systems

Sample number	OC kg m^{-3} soil	TCN kg m^{-3} soil	LF kg m^{-3} soil	LF-OC%	LF-N%	C/N Soil	C/N LF
VR1	15.1a[†]	1.75a	2.47a	25.4a	1.58a	8.6a	16.1b
RA1	14.1ab	1.61ab	2.46a	27.1a	1.31c	8.8a	20.7a
C1	11.4b	1.38b	2.23b	21.1b	1.40b	8.3a	15.0b
VR4	13.0b	1.55ab	4.12a	25.0a	1.43b	8.4a	17.5a
RA4	15.9a	1.71a	3.21b	26.3a	1.57a	9.3a	16.7a
C4	13.0b	1.48b	2.01c	23.5b	1.44b	8.8a	16.4a

[†] Different letters within columns (e.g., OC or TCN) indicate that treatment means were significantly different at the 0.05 level.

Table 3.3. Ratios of selected peak heights from DRIFT spectra of humic acids (Wander and Traina, 1996b)

HA samples	R_1 $\frac{1727+1650+1160+1127+1050}{2950+2924+2850+1530+1509+1457+1420+779}$	R_2 $\frac{1727}{1457+1420+779}$
VR1	0.57 ± 0.02b[†]	0.99 ± 0.01b
RA1	0.69 ± 0.01ab	1.24 ± 0.02a
C1	1.00 ± 0.01a	1.03 ± 0.01ab
VR4	1.18 ± 0.03a	0.91 ± 0.01a
RA4	0.84 ± 0.01b	0.61 ± 0.01b
C4	0.85 ± 0.01b	0.62 ± 0.01b

[†] Average ratio ± standard deviation. Different letters within each column indicate that treatment means were significantly different at the 0.05 level.

Table 3.4. Ratios of selected peak heights from DRIFT spectra of fulvic acids (Wander and Traina, 1996b)

FA samples	$\frac{1850+1650+1400+1080+560}{3340+2924+1535+1457}$
VR1	4.31 ± 0.04a[†]
RA1	1.09 ± 0.01c
C1	2.31 ± 0.03b
VR4	2.65 ± 0.02a
RA4	0.93 ± 0.01b
C4	1.05 ± 0.01b

[†] Average ratio ± standard deviation. Different letters within each column indicate that treatment means were significantly different at the 0.05 level.

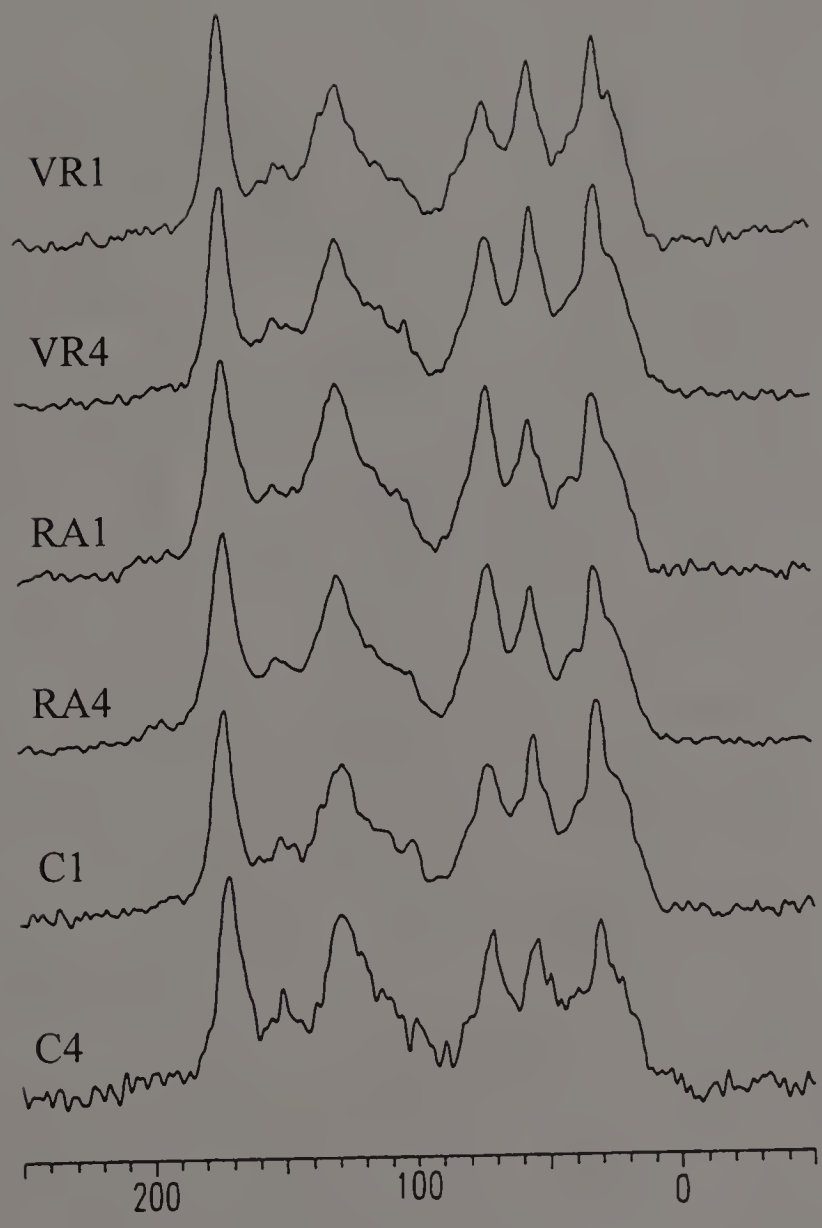
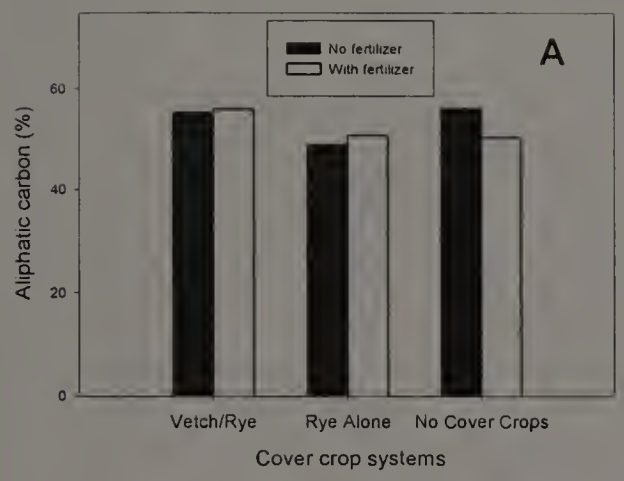
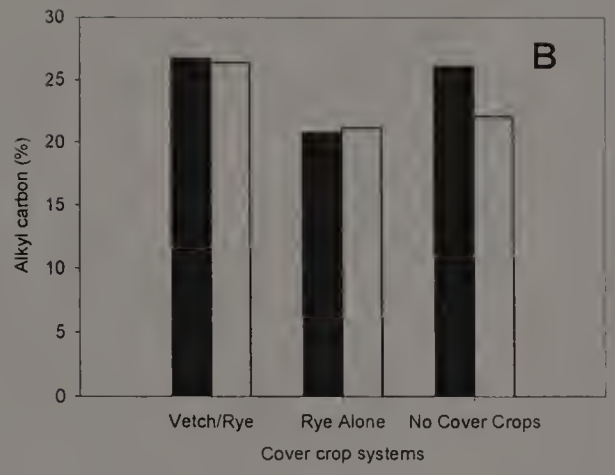
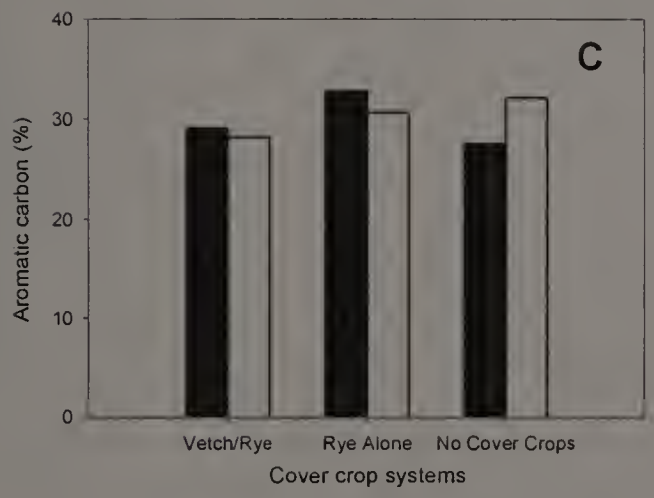


Figure 3.1 CPMAS-TOSS ^{13}C NMR spectra of HA extracted from different cover crop systems







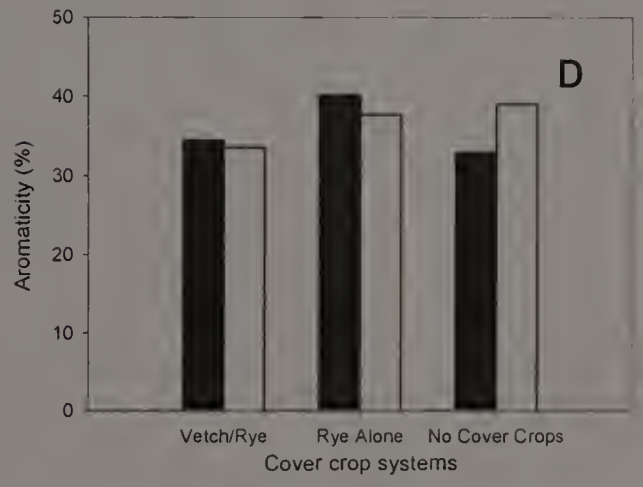


Figure 3.2 CPMAS-TOSS ^{13}C NMR data of HA

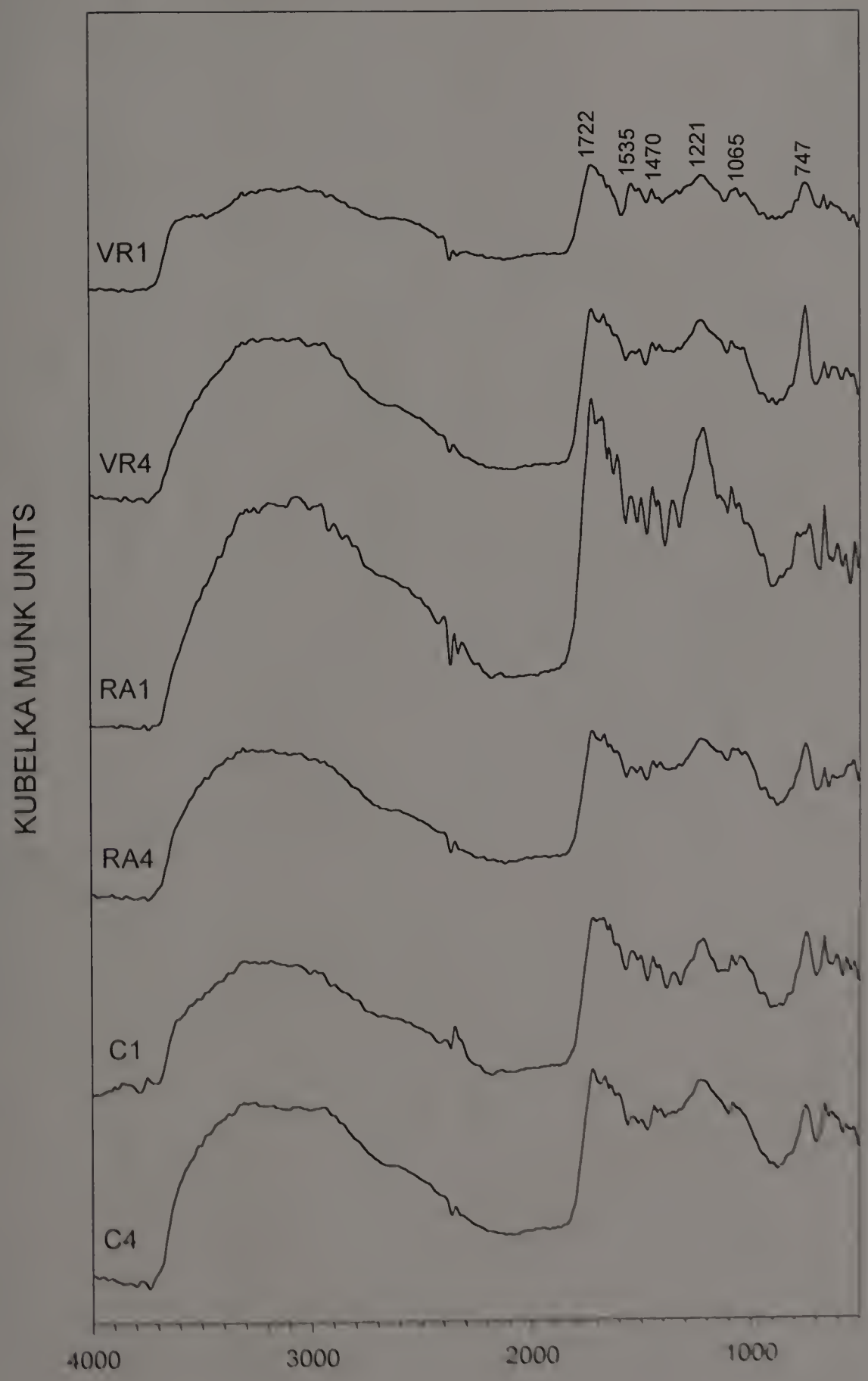


Figure 3.3 DRIFT spectra of HA

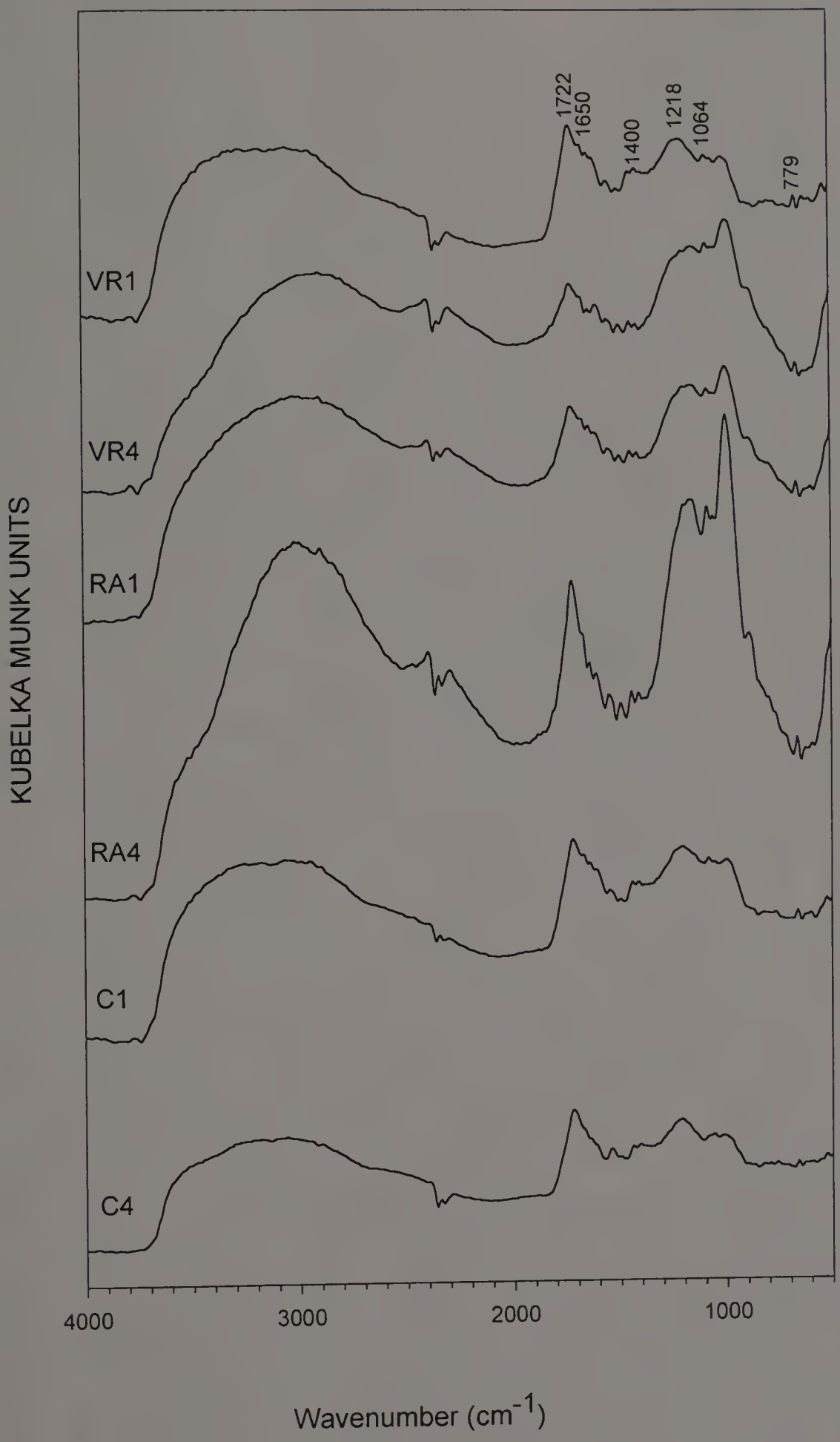


Figure 3.4 DRIFT spectra of FA

CHAPTER 4

LONG-TERM TILLAGE EFFECTS ON SORPTION AND DESORPTION BEHAVIOR OF METOLACHLOR

4.1 Abstract

Sorption and desorption are important processes that influence the amount of pesticides retained by soils. However, the detailed sorption mechanisms as influenced by soil tillage management are unclear. This study examined the sorption and desorption characteristics of metolachlor in a Norfolk soil. We used soil samples collected (1999) from the long-term conservation tillage (CnT) and conventional tillage (CT) research plot at Darlinton, SC. Humic acid (HA) was extracted and purified by International Humic Substances Society methods and humin was prepared by the methods of Preston and Newman (1995). Metolachlor sorption experiments were conducted using a batch-equilibrium method. Three desorption steps were carried out for a total desorption time of 9 days following the sorption experiments. Metolachlor hysteresis was observed for all soil and its organic matter fractions. Sorption nonlinearity *(N)* and hysteresis were dependent on structure and composition of soil organic matter (SOM). The *N* value of HA and humin from CnT was higher than that of the CT treatment, which may be related to high aromaticity of SOM fractions in the CT treatment. Sorption capacity was positively correlated with soil organic carbon (SOC) content. These results show that long-term tillage management can affect metolachlor sorption and desorption behavior greatly.

4.2 Introduction

Sorption/desorption is an important process that influences the mobility and bioavailability of hydrophobic organic compounds (HOCs) in soil environment. A number of soil properties have been shown to affect the retention of HOCs in the soil profile, including organic matter content, soil acidity, soil texture, Fe and A1 oxide content, and clay mineralogy (Johnson and Sims, 1993: Chefetz et al., 2000; Hundal et al., 2001). The retention and mobility of pesticides in soils are of particular importance in investigations related to their environmental fates and behaviors due to extensive use.

Soil minerals and SOM are the major components for sorption of organic chemicals including pesticides. The reactive mineral components are silicate clays and oxyhydroxides and amorphous materials of Fe and Al. Pesticide distribution patterns within soil are controlled by a complex series of equilibrium interactions between pesticides and soil components. Pesticides in the liquid phase are readily available for plant uptake and leaching. Pesticides sorbed to solid phases are generally regarded as being slowly available for plant uptake because of strong bonding forces and slow desorption kinetics. Agricultural practices generally do not substantially change contents and characteristics of soil mineral components due to their inert chemical nature, for example, there are no marked differences in clay contents between conservation tillage (CnT) and conventional tillage (CT) plots after 18 years (Novak et al., 1996). Thus, sorption by minerals would not vary much with agricultural practices. However, the change in quantity and quality (e.g.,

structures) of SOM by agricultural practices can be significant and may potentially alter sorption behavior, mobility, and biological activity of pesticides in soils.

Metolachlor is a pre-emergence herbicide used commonly in corn, soybean, and peanut in the USA and has been detected in surface and groundwater (Ritter, 1990; Maas et al., 1995). Information regarding the metolachlor sorption and desorption characteristics in soil is necessary to predict its fate in the soil environment. Evaluation of long-term tillage effects on pesticide sorption and desorption will be important to southeastern Coastal Plain soils, which are regarded as having a high pesticide leaching potential because of high precipitation amounts, sandy textures, and low SOM levels (Kellog, 1993). Seybold and Mersie (1996) investigated the sorption and desorption of metolachlor in two soils from Virginia and showed that differences in the composition of organic matter and/or the amounts of other components (e.g., clay) play a significant role in the sorption process. Johnson and Sims (1993) found a significant positive correlation between SOM and sorption of metolachlor ($r = 0.925$) and noted that the spatial variability of SOM was similar to that of metolachlor sorption coefficients. They further reported that the variability of sorption coefficients in a field soil could be more readily estimated by measuring the variability of SOM.

In our previous paper (Ding et al., 2002), we showed that tillage system affected the structure and composition of SOM in the southeastern USA Coastal Plain significantly. The objective of this study was to investigate the sorption and desorption behavior of metolachlor by different soil components (soil, humic acid,

or humin) and evaluate metolachlor sorption and desorption mechanisms as influenced by the long-term tillage systems.

4.3 Materials and Methods

Site description and sorbent preparation

Soil samples were collected from long-term conservation and conventional tillage research plots at the Clemson University Pee Dee Research and Education Center (Darlington, SC). Conservation tillage (CnT) completely eliminated disking and field cultivation for weed control. Conventional tillage (CT) consisted of multiple diskings (0-15 cm) and use of field cultivators (0-5 cm) to maintain a relatively weed-free soil surface and incorporate crop residues, fertilizers, and lime. The plots have been in several types of rotations including continuous corn, corn-wheat-soybeans, and corn-wheat-cotton. Detailed management practices were reported previously (Novak et al., 1996). A bucket auger was used to collect core from Ap horizon (0-15 cm), which was subsampled at three depths (0-5, 5-10, and 10-15 cm) at random locations within each plot and then composited, air-dried, and sieved (2 mm). However, only samples from two depths (0-5 cm, and 10-15 cm) were used in this study.

Humic acid (HA) was extracted, and purified by the methods of the International Humic Substance Society (Ding et al., 2001a). After separating the supernatant solution of $Na_4P_2O_7$ extraction, the residues (crude humin) were treated with HF (3.5% v/v) and a magnetic stir bar in a plastic bottle (Preston and Newman, 1995). The mixture in the bottle was stirred for 4 hours on a magnetic plate, and the stir bar was taken out to remove magnetic particles clinging to it.

After centrifugation, the supernatant was discarded and filled with fresh HF solution, and the stir bar was replaced. The HF treatment was conducted a total of 6 times, but the stir bar was only used for the first 3-4 treatments, as the yield of magnetic particles declined sharply with each treatment. After the last HF wash, the de-ashed humin was washed with deionized water three times before transferring into a shallow dish for air-drying. The C, H, and N contents of the isolated HA and humin were measured with a Fisons Model EA 1108 Elemental Analyzer in the University of Massachusetts at Amherst. Spectra of HA and humin were obtained by using the CPMAS-TOSS ^{13}C NMR techniques (Xing et al., 1999). Selected chemical properties of HA, and humin are listed in Table 1.

Sorption and desorption experiments

Metolachlor [2-chloro-N-(2-ethyl-6-methyphenyl)-N-(2-methoxy-1-methylethyl)] acetamide was purchased from the Crescent Chemical Company (Hauppage, NY) and ^{14}C-labeled metolachlor was from Ciba-Geigy Company (Greensboro, NC). Metolachlor molecular formula is $C_{15}H_{22}C1NO_2$. The *log Kow* (*Kow* = octanol/water partition coefficient) is 3.45 and solubility is 530 mg L^{-1}.

Sorption experiments were conducted using a batch equilibration method (Yuan and Xing, 2001) in 8-mL screw-cap vials with Teflon-lined septa. The background solution was 0.01 M $CaC1_2$ with 200 μg/mL $HgC1_2$ as a biocide. The ^{14}C-labeled metolachlor, along with its non-radioactive stock solutions, was mixed with sorbents (soil, HA, or humin) at different solid to solution ratios to achieve 30-70% uptake of solute. Nine different initial concentrations were used, which were evenly spaced on the log scale. The initial metolachlor concentrations ranged from

0 to 250 ppm. Each point was run in duplicate. Two blanks without sorbent were run for each initial concentration. The vials were agitated on hematology mixers, giving gentle rocking-rotating motions. After mixing, suspensions were centrifuged to obtain a clear solution. The solute in the solution was determined by liquid scintillation counting. A 3-day sorption experiment was used because preliminary sorption experiments showed no significant increase between 3-day and 7-day sorption, indicative of an apparent equilibrium at or before 3 days.

The background solution for desorption experiments was prepared as follows. We mixed 0.01 M $CaCl_2$ and 200 μg/mL $HgCl_2$ with test sorbents using the same solid to solution ratio as used in the sorption experiments, but without metolachlor. Then, the suspension was mixed at the room temperature for the identical length of time as the sorption or desorption experiment. After an appropriate period of mixing, the bottle was centrifuged at 3000 rpm for 30 minutes to collect the supernatant which was used later as the background solution for desorption experiments. By using this background solution, we expected to have replenished dissolved and colloidal substances lost (sorbent) in the discarded fluid, and thus ensured that the solution chemistry was not changed during desorption cycles (Xia and Pignatello, 2001).

The desorption experiments were conducted in sequential decant refill steps immediately following the completion of sorption experiments. At the end of sorption experiments, solids were separated from the aqueous solution by centrifugation at 3000 rpm for 30 minutes and an aliquot (1 mL) of supernatant was withdrawn from each vial for liquid scintillation counting. Then about 4 mL of the

remaining supernatant (depending on the sorbent) was replaced with the same volume of the background solution (as described above), by weight to the precise amount. After dilution, the vials were shaken on the hematology mixers for 3 days. The suspension was centrifuged and an aliquot (1 mL) of supernatant was extracted for analysis. The above process was repeated for two more cycles. The concentration of the test ^{14}C metolachlor present in the supernatant solution after each desorption was determined by liquid scintillation counting. Desorbed ^{14}C sorbate was calculated at each desorption stage. The amount of sorbate remaining on sorbent at each desorption stage was calculated as the difference between the initial sorbed amount and the desorbed amount.

All sorption and desorption data were fitted to the logarithmic form of the Freundlich equation:

$$logx/m = logK_f + NlogC \qquad (1)$$

where x/m ($\mu g/g$) is the sorbed concentration and C (μg/mL) is the final solution concentration. The K_f and N are the Freundlich coefficients, and the latter is often used as the index of isotherm non-linearity.

We used reduced concentration, C_r [solubility (S_w)-normalized solution concentration, $C_r = C/S_w$] to replace C in equation 1. The C_r is dimensionless. Then, K_f was converted to K'_f (modified Freundlich coefficient). The values of K'_f as calculated from C_r can be conveniently normalized to organic carbon (OC) content ($K'_{foc} = 100 * K'_f/\%OC$) (Carmo et al., 2000).

Desorption hysteresis was calculated as the ratio of Freundlich constants for desorption to sorption, i.e., N_d/N_s (subscripts d and s refer to desorption and

sorption, respectively) (Barriuso et al., 1994; Yuan and Xing, 2001). The lower the hysteresis index, the higher the degree of hysteresis (i.e., more difficult to desorb).

4.4 Results and Discussion

Sorbent properties

Organic carbon contents were 1.54% (0-5 cm) and 0.35% (10-15 cm) in the soil of CnT plots. For CT treatments, organic carbon contents were 0.85% (0-5 cm) and 0.54% (10-15 cm) respectively. The top soil (0-5 cm) of CnT contained significantly higher soil organic carbon (SOC) than that of CT treatment. As reported by Novak et al. (1996), the lack of mixing plant residue resulted in a build up of SOC in the top few cm of CnT in the Norfolk soil. Thus, twenty years of CnT management has resulted in an increase in the SOC in the top 0 to 5 cm layer of the unfractionated Norfolk soil. This result was consistent with the reports by Bruce et al. (1990) and Unger (1991) that CnT management can increase both the carbon content of the soil surface horizon and crop yield. Increased SOC, coupled with increased surface residues, can improve soil productivity by increasing capture and infiltration of water and reducing erosion (Langdale et al., 1992).

The HA from the top soil (0-5 cm) of CnT management contained higher aliphatic-C (0-108 ppm) and lower aromatic-C (108-162 ppm) than that of CT plots (Table 1). The humin fractions showed the same trend as observed for HA. This observation is consistent with the enhanced decomposition of plants residue in the CT plot. Previously, we also examined O/R ratios (reactive oxygen-containing to recalcitrant functional groups), based on the peak heights generated from DRIFT spectra (diffuse reflectance infrared Fourier transform). The high O/R ratio of HA

was observed in the top soil (0-5 cm) of CnT, indicating that SOM was more biologically active (Ding et al. 2002). Compared with humin, HA was derived mainly from more recent vegetation input. Humin is usually regarded as remnants of the decomposition of SOM fraction which associated or encapsulated by minerals (Baldock and Skjemstad, 2000). Thus, humin exhibits a more recalcitrant structure than HA.

Metolachlor sorption

Metolachlor chemical degradation in soil environment is negligible (Zhu and Selim, 2000). Although studies, both field and laboratory, indicate that metolachlor half-life values are highly dependent on the experimental conditions (Chesters et al., 1989), microbial degradation of metolachlor would be minimal in this study because 200 μg/mL $HgC1_2$ was used in all our experiments. Thus, the metolachlor degradation will not be addressed here.

Sorption of metolachlor by soil, HA, and humin from CnT and CT treatments is shown in Figures 4.1 and 4.2 respectively. The detailed metolachlor sorption parameters are listed in Table 2. Sorption of metolachlor by soil, HA, and humin was well described by the Freundlich model (Figs. 1 and 2, Table 2). Sorption of metolachlor was nonlinear ($N < 1$) for all soil, and SOM fractions in this investigation.

Sorption of metolachlor was much higher by the soils that contained high amounts of organic carbon than by the soils containing low organic materials (Tables 4.1 and 4.2). Those results were in agreement with the report by Novak et al. (1996). They, after characterizing the impact of two different tillage systems

(CnT vs CT) on sorption of atrazine and fluometuron in plots of Norfolk loamy sand soil, demonstrated that tillage and depth affected SOC contents in the tillage systems. Thus, atrazine and fluometuron sorption was significantly different with tillage system and soil depth. Correlation analyses between organic carbon and modified sorption coefficient (K'_f) showed that sorption of metolachlor was highly related (r = 0.93) to the amount of organic materials in the soil, HA, or humin fractions. Previous investigators also indicated that metolachlor sorption by soils was related to organic carbon and clay contents of soils (Kozak et al., 1983; Peter and Weber, 1985). Similarly, Carmo et al. (2000) reported that sorption of naphthalene and phenanthrene is a function of organic carbon for heterogeneous soil materials and their components.

Again, when we compared K'_{foc} values (K'_f normalized to the organic carbon content), for the same treatment (Table 2), K'_{foc} was larger in humin than that of HA. Differences between K'_{foc} values may suggest that organic matter in humin had a greater impact on sorption of metolachlor than in HA. One possible interpretation is that the characteristics of the organic matter (e.g., aromaticity) varied (Table 4.1) among the organic fractions and could lead to differences in sorption capacity. However, K'_{foc} values of both HA and humin were larger than soil, which was probably caused by the structural comformation changes during the extraction processes. After the removal of the non-mineral bound organic matter fractions (i.e., fulvic acid and HA), humin may show more exposed sorption sites. Similarly, by changing the chemical and physical conformation, HA might take more "expanded and open" structures which are accessible to metolachlor

molecules. By investigation of 1-naphthol sorption with different organic matter fractions of several soil samples, Salloum et al. (2001) reported that organic matter physical conformation and accessibility are important in contaminant sorption. Similarly, they observed the increase in sorption after removal of HA and fulvic acids.

The metolachlor sorption isotherms (Figs. 4.1 and 4.2) were characterized by different *N* values (Table 2). For the same treatment, *N* values followed the order: HA > soil > humin. As an example, the order for top layer (0-5 cm) of CT plots was HA (0.884) > soil (0.853) > humin (0.815). This order was as predicted from the dual-mode model in according to the compositions of these fractions, i.e., reflecting the order of glassy nature of the organic matter. Higher *N* values in HA (i.e., smaller deviation from linearity) for metolachlor sorption may indicate that the degree of HA heterogeneity in terms of sorption sites was less as compared with humin fractions. More specifically, after $Na_4P_2O_7$ extraction of soil, the loosely bound fractions (HA and fulvic acid) were removed and more condensed fractions (humin) were left behind. Therefore, more competition and less linear isotherms were observed in humin fractions, which was explained using the dual-mode sorption model (Xing and Pignatello, 1997). By study sorption of low-polarity compounds in glassy poly(vinylchloride) and SOM, Xing and Pignatello (1997) reported that the *N* values for 1,2-dichlorobenzene and 1,3-dichlorobenzene declined in the following order: peat-HA > peat > peat-humin.

Metolachlor desorption

Results of metolachlor desorption by soil, HA and humin are shown in Figures 4.3, 4.4, and 4.5 respectively. Desorption isotherms of metolachlor for all different sorbent systems were constructed using 3 consecutive desorption cycles corresponding to initial concentrations. Both the duplicates for each experiment were reported on the isotherms. All the data fitted well with the Freundlich model. Hysteresis was observed in all our isotherms.

Desorption is commonly observed to be biphasic, involving a relatively fast initial release of sorbed solute followed by a prolonged and increasingly slower release as desorption proceeds, indicating the possibility that some fractions of solute may be irreversibly bound to soil components (Weber et al., 1998). Hysteresis is thought to be originating from two sources: site specific binding and physical trapping. The amount desorbed during the course of our three successive desorption steps may represent the sum of readily desorbable or weakly retained metolachlor fractions. Differences of hysteresis between different initial concentrations and between different sorbents were observed in our study. For example, at the lower initial concentrations, the desorption isotherm N values were smaller than that of higher concentrations for all three different sorbents of both tillage systems (soil, HA, and humin) (Figs. 4.3, 4.4, and 4.5). This is as expected, because there were only a limited number of high energy sites in SOM, they would be filled first and the proportion of metolachlor molecules in these sites was higher at lower concentrations. On the other hand, at high concentrations, the limited high-energy sites were saturated (resistant fraction) and the proportion of resistant

fractions would be lower at high concentrations than that at lower concentrations, thus, overall desorption was easier. However, at the highest concentration, the N values of metolachlor desorption isotherm for all our experiments tended to decrease. This may be due to the creation of more holes or sorption sites upon the removal of metolachlor molecules. Xia and Pignatello (2001) reported as the concentration increase, the sorbate causes dilation (swelling) of the sorbent, then, converting the glassy phase to the rubbery phase. With subsequent desorption due to the removal of sorbate molecules, these new holes can trap more sorbate molecules, which are resistant to desorption. Consequently, at the highest concentration, the desorption isotherms for all three sorbents became more nonlinear as compared to previous few concentration points (Figs. 4.3, 4.4, and 4.5). We surmised that the first eight initial concentrations might not be high enough to alter SOM matrix and create new sorption sites.

Comparisons of hysteresis index of soil, HA, and humin from CnT and CT treatment are shown in Figures 4.6, and 4.7 respectively. The hysteresis index followed the HA < soil < humin order. Compared with HA, humin had a relatively more rigid structure (rich in glassy or condensed phase), corresponding to maximum hysteresis.

The hysteresis index for both HA and humin was higher in CnT treatment than that of CT plots. For example, at the initial concentrations of 10, 60, and 150 (μg/mL) for metolachlor, the hysteresis index for HA in CnT plots was 0.144, 0.266, and 0.283 respectively, while for CT, it was 0.128, 0.242, and 0.256 respectively. After investigation of sorption/desorption of naphthalene,

phenanthrene, and α-naphthol by cation-saturated HA, Yuan and Xing (2001) showed that there was a good correlation ($r^2 > 0.90$) between hysteresis index and *N* values of sorption isotherms. This correlation is anticipated because the same sources may cause both sorption nonlinearity and hysteresis. In another study, Xing (2001a) reported that the *N* values of naphthalene and phenanthrene sorption decreased proportionately with increasing aromaticity of HA. Thus, low hysteresis index in CT treatments may be caused by the relatively high aromatic carbon contents (Table 1). Based on a solid-state ^{19}F-NMR study on hexafluorobenzene (HFB) sorption by sediments, Cornelissen et al. (2000) reported that HFB in sediment at rapidly desorbing sites showed a resonance at –125.5 ppm relative top $CFC1_3$, whereas HFB at slowly desorbing sites showed a resonance at –165.6 ppm. They concluded that the differences in desorption kinetics are related to differences in sorption status. Rapidly desorbing solute shows linear sorption, whereas the slowly desorbing solute fractions show Langmuir type non-linear sorption. All these results are in line with the dual-mode sorption model of SOM (Xing, 2001b; Yuan and Xing, 2001).

It is obvious from the above observation that the most likely cause of metolachlor hysteresis is to be irreversible or slowly reversible sorption. This is supported by the results reported by Zhu and Selim (2000). It is most likely that the sorbed metolachlor molecules with the lowest site energy came into solution at the beginning of desorption. However, desorption will become increasingly difficult with increasing number of desorption steps because of the resistance of the molecules sorbed in energetic sites.

In conclusion, nonlinear sorption isotherms for metolachlor were observed in all soil samples and their organic fractions (HA and humin for CnT and CT treatments). The *N* value of HA and humin from CnT1 was higher than that of CT1, which may be caused by high aromaticity of SOM fractions in the CT1 treatment (Xing, 2001a). The order of sorption capacity was humin > HA > soil. The hysteresis index of both HA and humin in CnT plots was higher than that of CT treatment. For the same treatment, the hysteresis followed the HA < soil < humin order.

Table 4.1. Chemical property of sorbents

	C (%)	Aliphatic-C (%) (0-108 ppm)	Aromatic-C(%) (108-162 ppm)	Aromaticity[†] (%)
HA CnT1[‡]	51.2	58.9	28.2	32.4
HA CT1	53.2	52.6	31.8	37.7
Humin CnT1	7.18	47.9	34.1	41.5
Humin CT1	7.82	40.4	47.7	54.1

[†](108-162 ppm)/(0-162 ppm)
[‡]1 referring to 0-5 cm depth

Table 4.2. Sorption parameters of metolachlor in soil and its SOM fractions

Sample	N	$logK_f$ $(\mu g\ g^{-1})\ (\mu g\ mL^{-1})^{-N}$	K'_f $(\mu g\ g^{-1})$	K'_{foc} $(\mu g\ (g\ of\ OC)^{-1})$
Soil				
CnT1[†]	0.866 (0.006)	0.55	578	37532
CnT2[‡]	0.811 (0.007)	0.10	199	56857
CT1	0.853 (0.005)	0.31	356	41882
CT2	0.835 (0.005)	0.14	289	53518
HA				
CnT1	0.962 (0.008)	2.08	49888	97438
CT1	0.884 (0.005)	2.14	35398	66538
Humin				
CnT1	0.841 (0.007)	1.68	9440	131476
CT1	0.815 (0.007)	1.64	7311	93491

[†]1 referring to 0-5 cm depth
[‡]2 referring to 10-15 cm depth

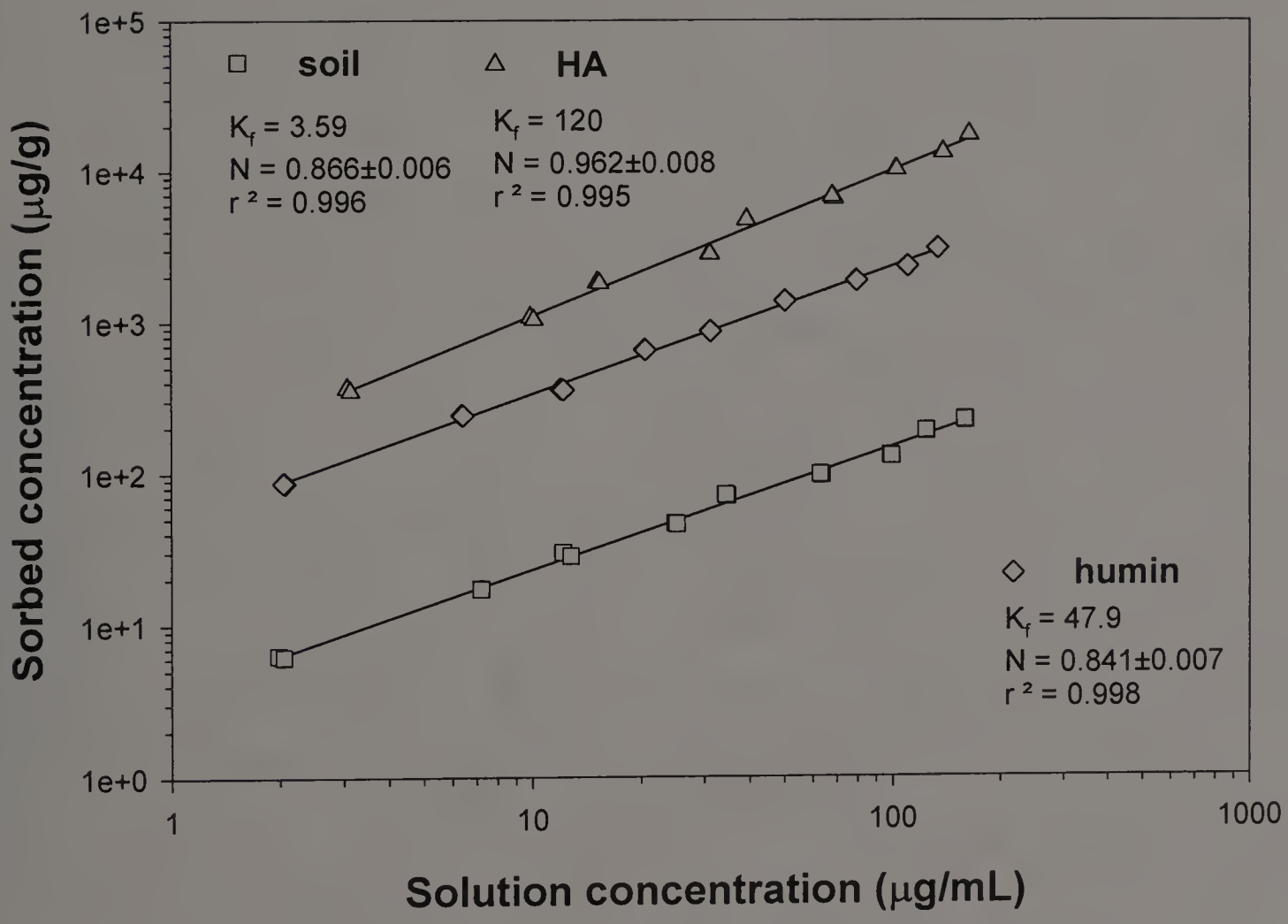


Figure 4.1 Sorption isotherm of metolachlor in soil, HA, and humin (CnT1)

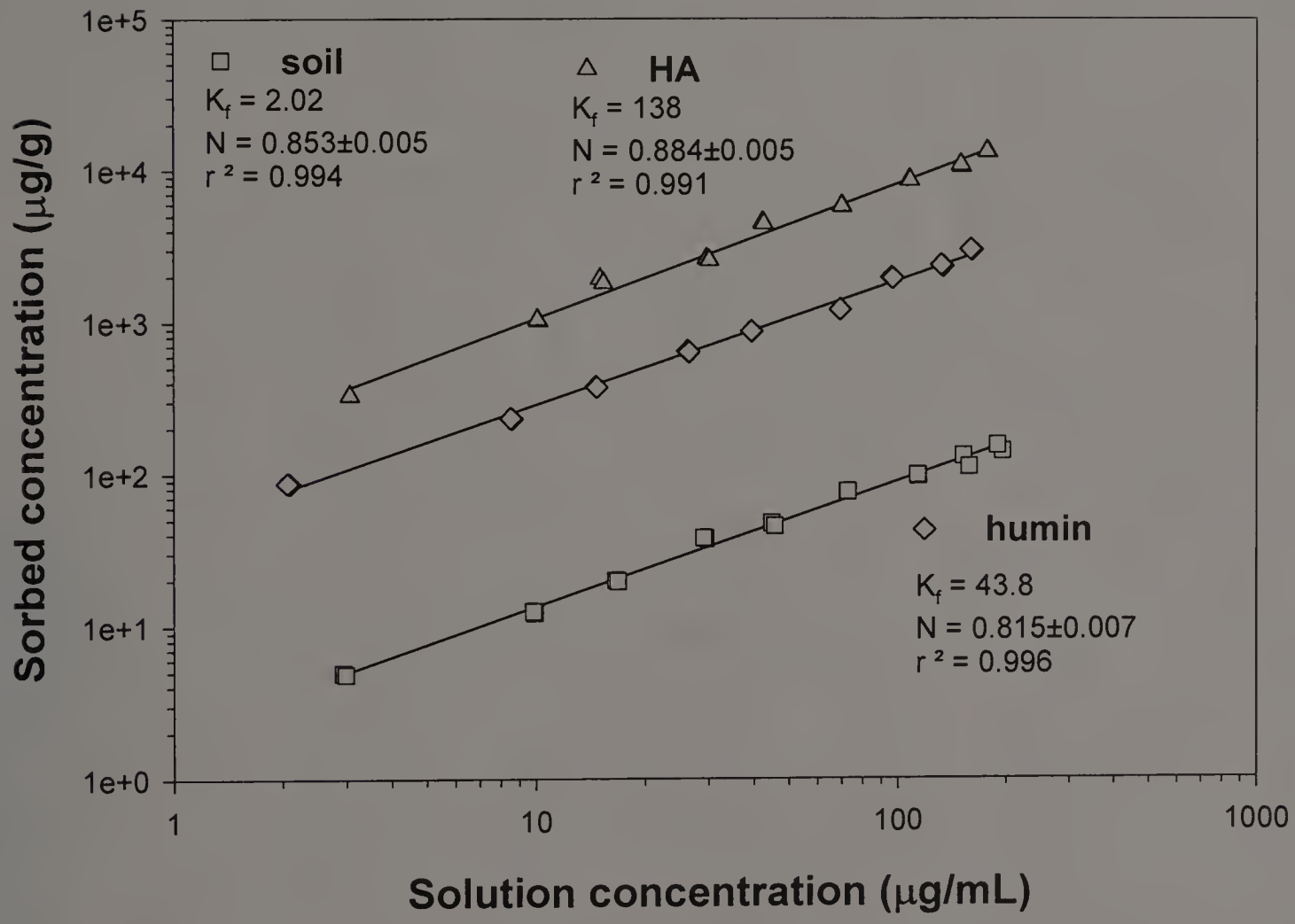


Figure 4.2 Sorption isotherm of metolachlor in soil, HA, and humin (CT1)

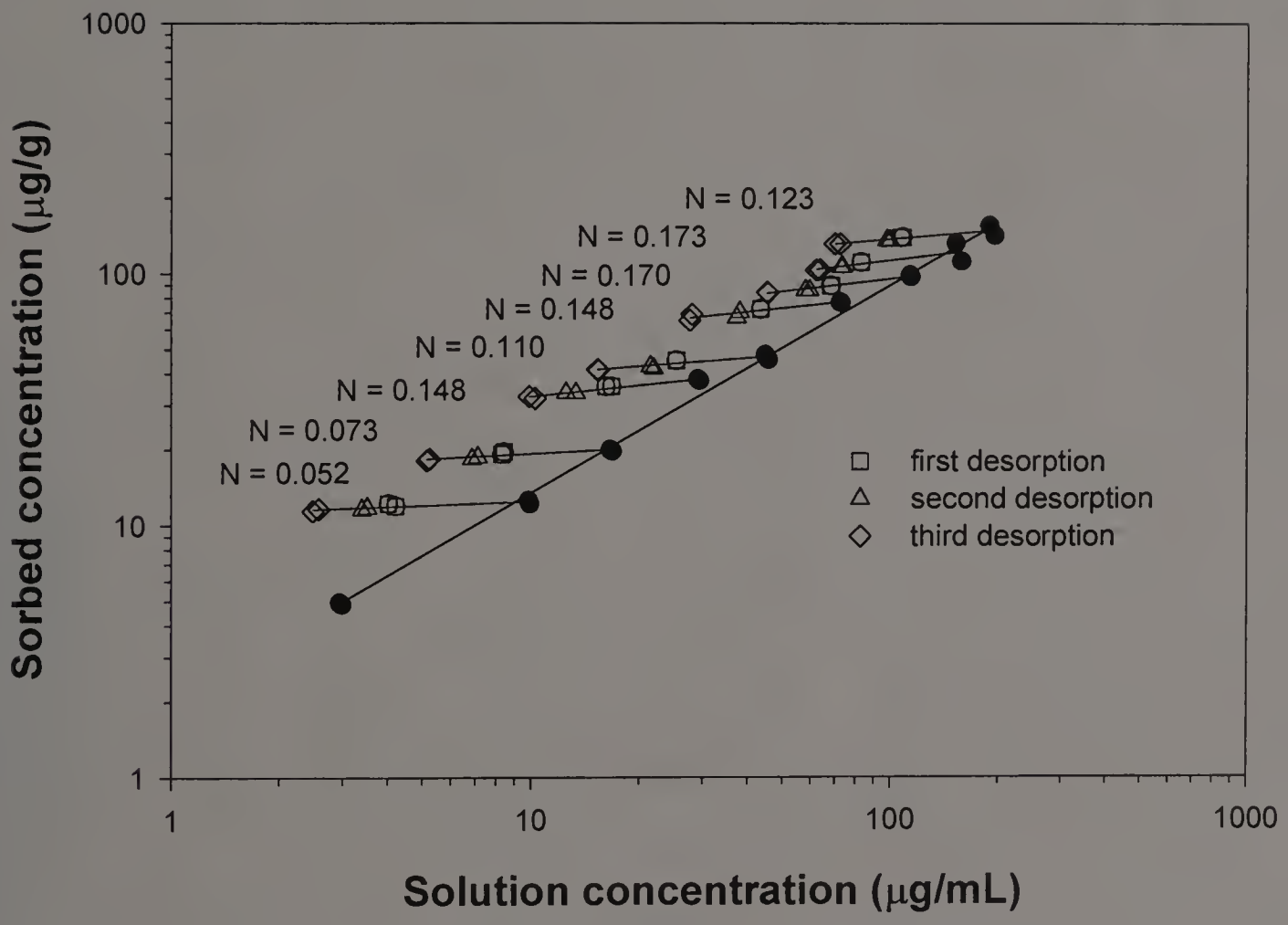


Figure 4.3 Sorption-desorption of metolachlor in soil (CT1)

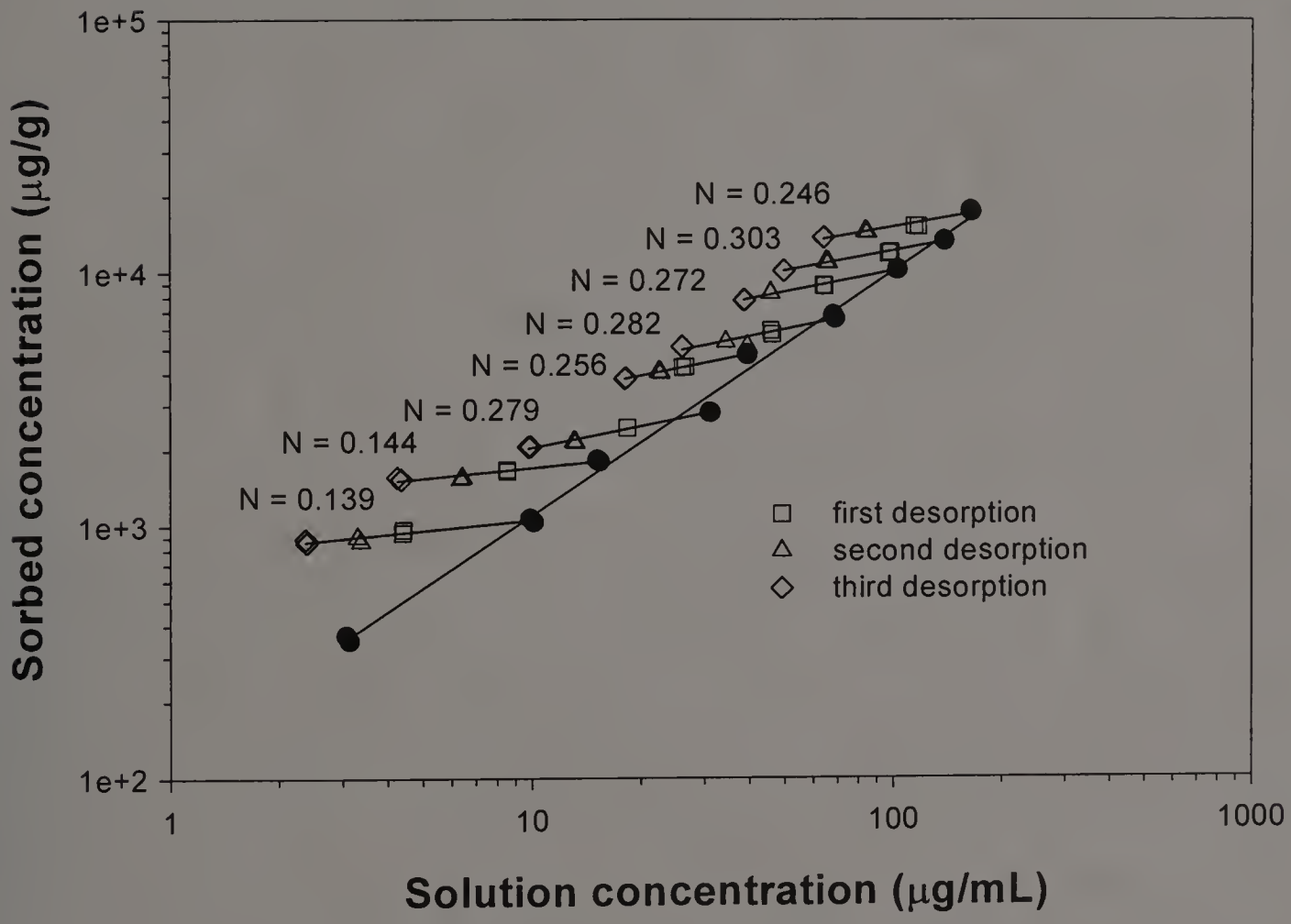


Figure 4.4 Sorption-desorption of metolachlor in HA (CnT1)

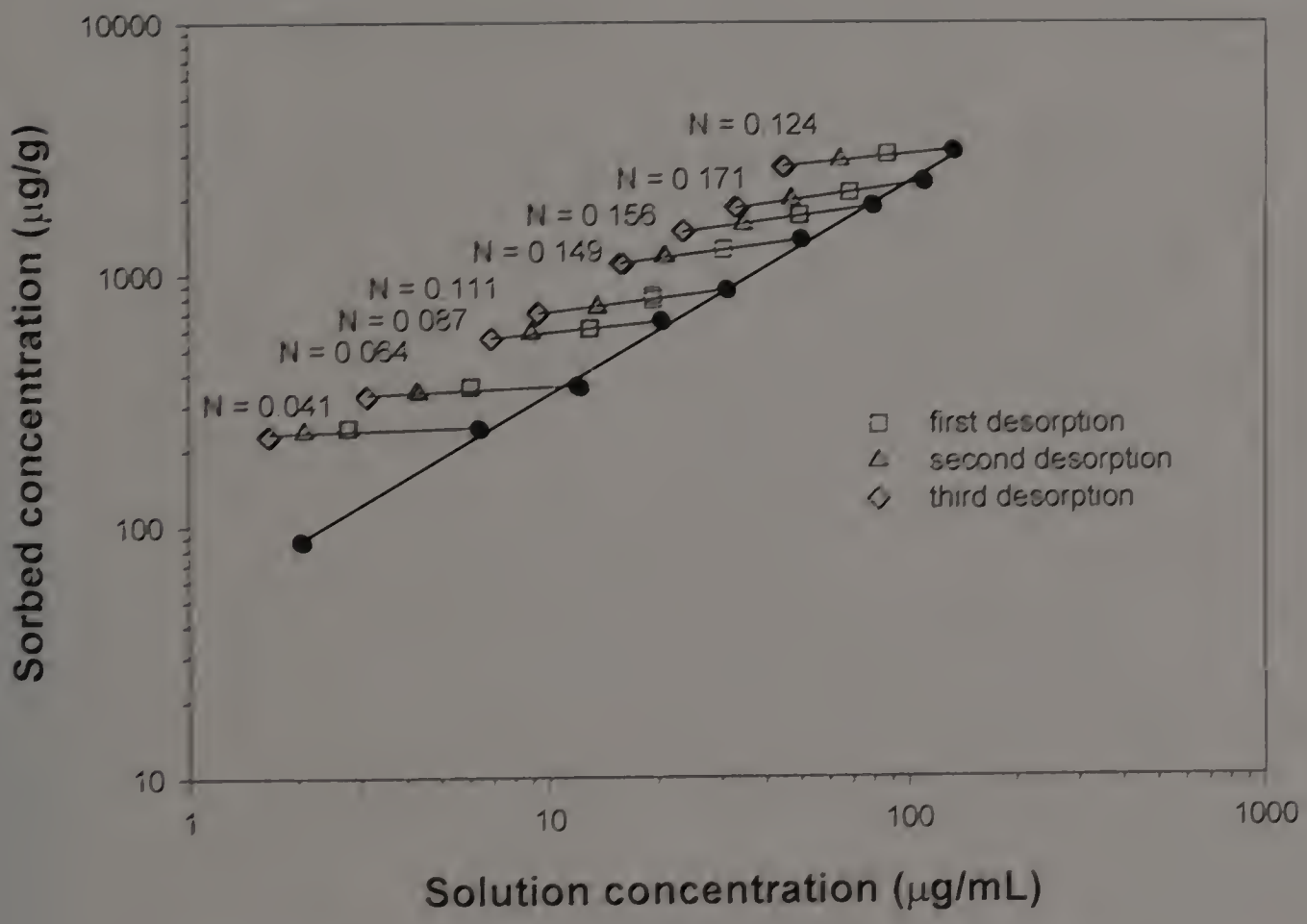


Figure 4.5 Sorption-desorption of metolachlor in humin (CnT1)

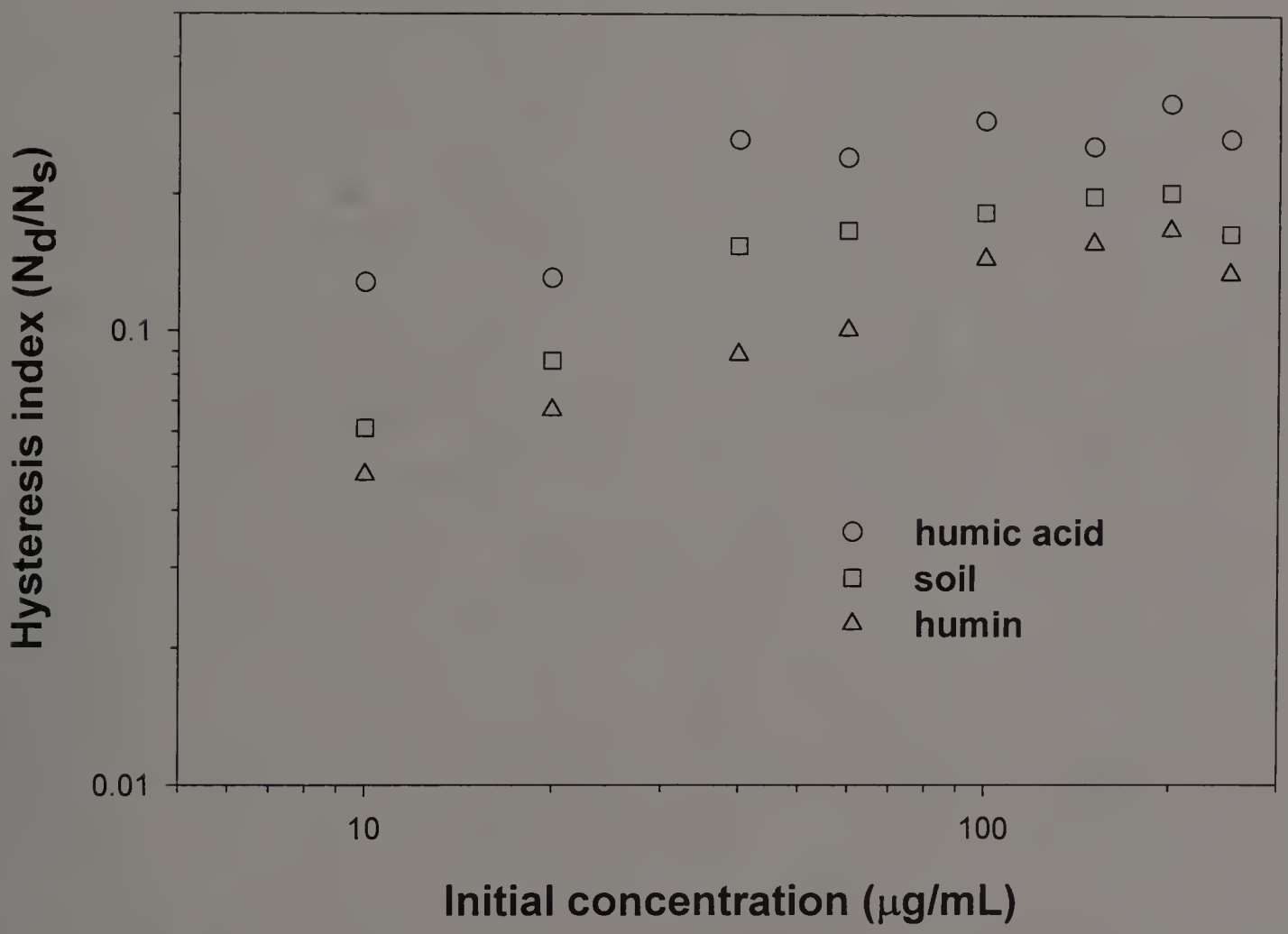


Figure 4.6 Comparison of hysteresis index of soil, HA, and humin fractions (CT1)

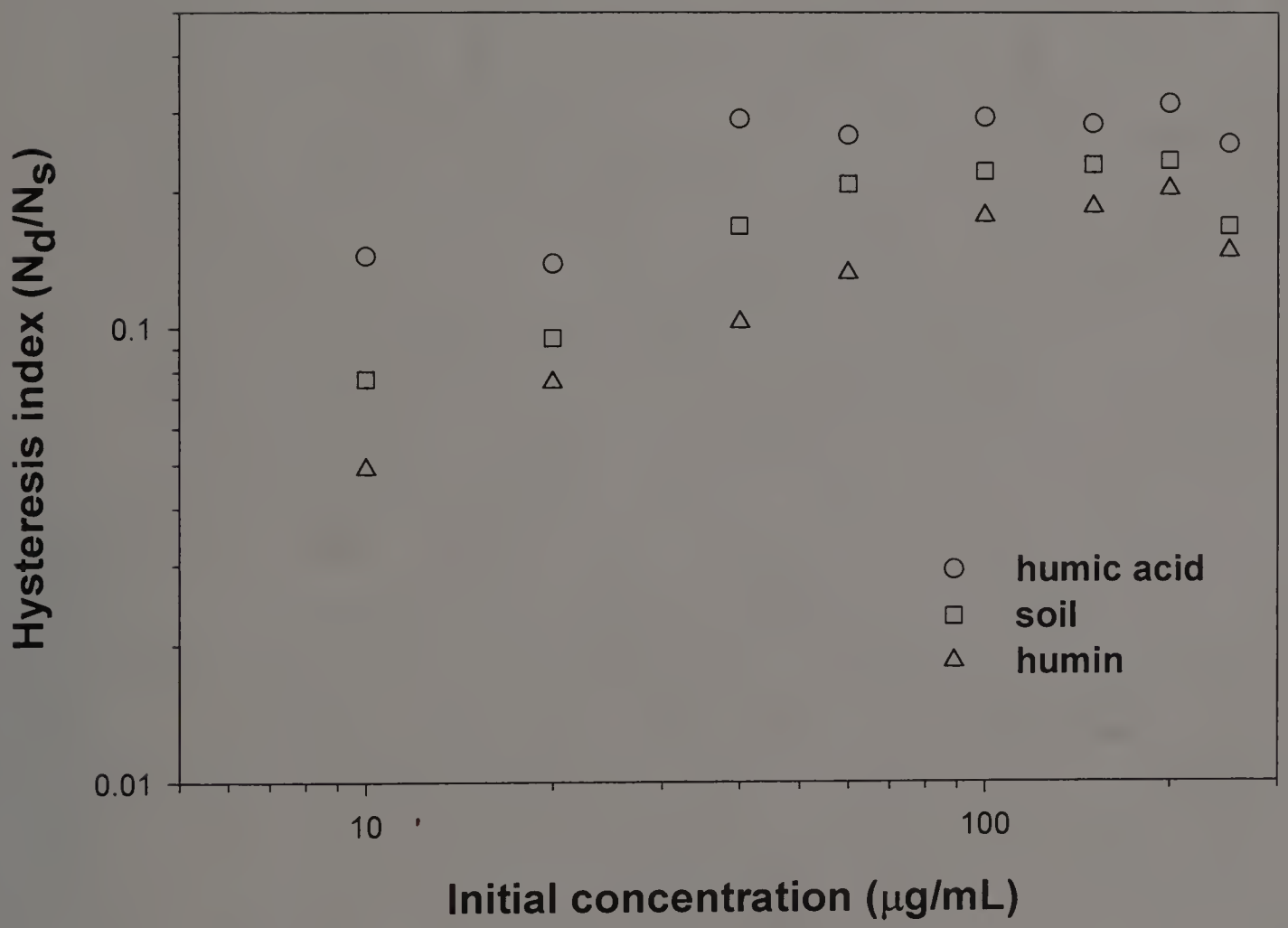


Figure 4.7 Comparison of hysteresis index of soil, HA, and humin fractions (CnT1)

APPENDIX

MODIFIED FREUNDLICH EQUATION PARMETER'S CALCULATION

All sorption/desorption data were fitted to the logarithmic form of Freundlich equation:

$$\log q_e = \log K_f + N \log C_e \qquad (1)$$

where q_e and C_e are sorbed (μg/g) and solution (μg/mL) concentration respectively. K_f and N are Freundlich constants. Equilibrium isotherms were plotted by log q_e vs. log C_e. The ratio of Freundlich exponents for desorption and sorption, i.e., N_d/N_s (subscripts d and s refer to desorption and sorption, respectively), has been considered as the hysteresis index (Yuan, 1999). The N_d/N_s values were calculated for all the systems of this study.

A dimensional analysis of equation 1 shows that the units of K_f vary nonlinearly with N. For example, if C_e is given in μg mL^{-1} and q_e is given in μg g^{-1}, then, K_f will be expressed in $\mu g^{(1-N)}$ g^{-1} mL^N. Therefore, K_f values derived from sorption isotherms with different N values cannot be directly used to compare sorption behavior of different sorbents. Although the absolute value of K_f equals the value of q_e (i.e., sorbent concentration) at $C_e = 1$, the units of K_f differ significantly from those of q_e. In addition, the absolute value of C_e depends on choice of units so that $C_e = 1$ could refer to a concentration outside the solubility limits of the solute (Carmo et al., 2000). Therefore, in order to compare the sorption characteristics of heterogeneous sorbents using unit-equivalent Freundlich coefficients. We may use the supercooled liquid state solubility (S_{scl}) to calculate C_r as follows:

$$C_r = C_e / S_w \qquad (2)$$

where C_r is solubility-normalized equilibrium concentration or reduced concentration. S_w is the aqueous solubility value for a given sorbate. The value of S_w is constant for a given temperature and is expressed in the same units as C_e. Thus, the ratio C_r is dimensionless. We can modify Freundlich equation as:

$$q_e = K'_f C_r^{\ N} \tag{3}$$

in which K'_f is the modified Freundlich coefficient and has the same units as q_e, e.g., μg g^{-1}, and its magnitude is equal to the value of q_e at $C_r = C_e/S_w = 1$. Thus, K'_f represents the mass of HOC sorbed per unit mass of sorbent when the C_e concentration approaches saturation, regardless of the choice of units. K'_f has units that are independent of the values of N, thus allowing direct comparison of sorption data for different sorbents. This approach yields a Freundlich coefficient, K'_f, that has both physical significance and meaningful units in addition to providing a flexible choice of units for C_e (Carmo et al., 2000).

The S_{scl} values for naphthalene, atrazine, and metolachlor at the equilibrium temperature (T) can be estimated from the melting point (T_m), S_w, and the heat of fusion (ΔH_f) by using the following equations (Chiou and Schmedding, 1982; Schwarzenbach et al., 1993):

$$\log(f_s / f_L) = (-\Delta H_f / 2.303RT_m)/(T_m / T - 1) \tag{4}$$

$$S_{scL} = S_w / (f_s / f_L) \tag{5}$$

where R is the gas constant and f_s and f_L are the fugacities of the crystalline solid and the supercooled liquid-state, respectively. Absolute temperatures must be used in equation 4. Alternatively, the entropy of fusion, ΔS ($\Delta S = \Delta H_f/T_m$), can be used in equation 4 to calculate the ratio f_s/f_L.

Although heat of fusion can be measured experimentally, it has not been found possible to estimate this parameter directly from considerations of chemical structure (Yalkowsky, 1979). Yalkowsky (1979) showed that for substituted benzenes which do not have conformational flexibility, the entropy of fusion falls within the range of 13.5 ± 3 cal/mole °C and that symmetry, dipole moment, and hydrogen bonding have little or no effect on ΔS. Estimation methods for ΔH have been given by Lyman et al. (1990) for organic molecules of intermediate size. If ΔH is not available for a compound of interest, the following equation may be used:

$$\ln(f_s / f_L) = 6.54(T - T_m) / T \qquad (6)$$

the basis for this approximation is an average value of 13 cal/mol °C for ΔS assumed for all organic compounds, and $\Delta H = T_m \Delta S$.

As the heat of fusion is rarely available, Mackay and Shiu (1977) used a simplified form of the f_s/f_L equation for correlation purposes:

$$\ln(f_s / f_L) = K(T_m - 298.15) \qquad (7)$$

where K is a constant (-0.02273), T_m is the melting point of the compounds. The basis of this equation assures that the entropies of fusion of the polynuclear aromatic hydrocarbons are approximately equal.

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